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TEXTILE RESEARCH JOURNAL

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The Measurement of Tearing Strength of Textile Fabrics[1]

L. H. Turl

Defence Research Medical Laboratories, Toronto, Ontario, Canada

Abstract

Current versions of two methods commonly used for the determination of tearing strength require clarification regarding treatment of the data obtained and revision to accommodate newer types of inertialess testing machines. Experimental information, providing the necessary background data, has been obtained. Sixteen fabrics of military interest have been tested by the Tongue (single rip) method and the Trapezoid method, on both pendulum and inertialess testing machines. The experimental data for these fabrics are analyzed to permit a comparison of both methods and both machines.

It is concluded that existing test method procedures are vague in respect to the interpretation of the data obtained, and results given by the two types of testing machine differ significantly. The Trapezoid method could be interpreted equally well through a single maximum tearing force for each specimen, but the Tongue (single rip) method is the more satisfactory experimental procedure.

It is suggested that the latter be utilized in specifications governing fabric procurement. The question of the relationship between existing tearing-strength test methods and service conditions and requirements is raised.

1. Introduction

It is well known that a tear frequently terminates the service life of a garment or textile item, either because the repair cannot be made economically or because the original appearance of the garment cannot be restored. At best, a patch of some kind may be attached over the torn area, restoring some or most of the original utility. Considerable importance is to be associated with the tearing strength, or resistance to tearing, of fabrics whose service life exposes them to this kind of damage. Most clothing falls into this category.

A variety of methods for the measurement of resistance to tearing is found in the literature. Millard [5] lists the main published methods prior to 1947, some of which were reviewed and compared briefly by Creswick [1]. Current interest in North America centers around two methods for tearing strength, namely, the Tongue (single rip) method and the Trapezoid method. The Pendulum method (Elmendorf) is also in use and provides essentially a measure of the energy required to produce a tear of unit length under the conditions of the test.

The Schedule of Methods of Testing Textiles (4-GP-2), published by the Canadian Government Specifications Board, contains the Tongue and the Trapezoid methods, as do also the U.S. Government Federal Specification CCC-T-191b and the A.S.T.M. Standards on Textile Materials, prepared by

[1] DRML Report No. 69-1, (PCC No. D49-75-70-05).

A.S.T.M. Committee D-13. In December 1952, the Canadian Government Specifications Board, recognizing the need for revision of test methods, set up a subcommittee to revise the existing Schedule of Methods for Testing Textiles (4-GP-2). The present study was carried out in connection with the revision of Method 12 (Tearing Strength) as presented in the Canadian Schedule.

2. The Problem

In general, the determination of tearing strength is subject to certain difficulties of interpretation of data. These difficulties are apparent in the following excerpts from various published sources, concerning the Trapezoid method, in which various approaches to the problem of interpretation are inferred.

A.S.T.M. (D-39-49): ". . . the average load necessary to tear the fabric shall be observed. . . ."

Garner, "Textile Laboratory Manual," p. 150: "The highest peak load is taken as the tear strength." (Possibly quoting Creswick [1].)

C.G.S.B. 4-GP-2 (December 31, 1952): "The average load necessary to tear the specimen is determined from the load maxima on the stress-strain curve."

U.S. Federal Specification CCC-T-191b (Method 5136): "The tearing strength of the specimen shall be the average of the five highest peak loads of resistance registered for 3 in. of separation of the tear."

U.S.Q.M., "U.S. Textile Test Methods." [6] (Fourth Commonwealth Conference, London, 1953); "U.S. specifications seldom require use of the Trapezoid method. It is especially applicable where . . . fabrics, because of unequal strength in warp and filling direction, cannot be tested by the Tongue (single rip) test. The nature or manner of tear caused by the Trapezoid method renders it less desirable for standardization purposes."

The Trapezoid method is not recognized in Handbook 11 of the British Standards Institution. The difficulty in interpreting the data which it provides is probably associated with the nature of the information it gives, which in turn depends upon rather complex and continuously changing geometry of the specimen under test.

The Tongue method suffers less from the problem of interpretation, since the essential geometry of the test remains unchanged as the tearing proceeds. Nevertheless, a comparison of the above-quoted sources [see Sec. 4*b*, Tongue (single rip) test] reveals that clarification of the treatment of the data, obtained usually in the form of an autographic record, is required.

In revising properly the text of the methods for tearing strength measurement in Schedule 4-GP-2, it was desired to ascertain

a. Whether either of the methods alone would suffice for the purposes of the schedule

b. Whether either method was superior to the other in any important respect

c. Whether, by either test method, the same results

Chart I. Identification of Fabrics

No.	Name	Weave	Weight (oz./sq. yd.)	Ends × Picks	D.N.D. (Canada) Specification
1	Nylon X36	Plain	8.0	41 × 41	
2	Nylon taffeta	Plain	2.6	155 × 85	Text. 7- 1-1
3	Cotton poplin	Plain	4.5	100 × 42	Text. 1- 6-3
4	Cotton combat	1/3 Z twill	9.7	114 × 65	Text. 1-14-9
5	Worsted serge	2/2 Z twill	9	63 × 54	Text. 2- 2-1
6	Wool-filled serge	2/2 Z twill	10.75	64 × 40	Text. 3- 2-1
7	H. T. Acetate (Fortisan)	2/1 twill	2.4	85 × 85	Text. 4- 5-1
8	Rayon twill	2/2 Z twill	3.75	115 × 67	Text. 4- 1-3
9	Melton		20	36 × 34	
10	Cotton lining	Plain	4	55 × 55	Text. 1- 5-1
11	Cotton utility	Plain	5.25	48 × 42	Text. 1- 3-1
12	Nylon canvas	Plain	5.75	105 × 80	Text. 7- 1-2
13	Cotton No. 8 duck	Plain	18	33 × 26	Text. 10- 1-1
14	Cotton	Plain	8.3	64 × 52	
15	Cotton drill	4/1 satin	9.5	92 × 60	Text. 1-14-8
16	Cotton drill	3/1 S twill	7.0	72 × 56	Text. 1- 5-3

would be obtained on both the newer types of inertialess tensile testing machines (Instron, Tinius Olsen, etc.) and the older conventional pendulum-type tensile testing equipment (Scott, Suter, Goodbrand, etc.)

3. Experimental Approach

Sixteen fabrics of current military interest were selected for use in a study designed to furnish answers to these questions. These fabrics were identified as shown in Chart I.

From each fabric specimens were cut according to the pattern shown in Figure 1. Weft tearing strength alone was considered adequate for the objectives of the study, and warp tearing tests were therefore not carried out. It will be noted from Figure 1 that the test specimens were prepared in groups of four, such that the same weft yarns were contained in two specimens for the Trapezoid test and two for the Tongue test. In this way a comparison of both test methods and both types of testing machine was permitted.

The various specimens, numbered as shown, were divided on the basis of random numbers into two groups, one for test on each type of machine, it being noted that Trapezoid and Tongue specimens bearing the same number were tested on the same machine. In this way similar random sets of six specimens were prepared, each set comprising specimens containing the same weft yarns as specimens of the other sets.

The tensile testing machines employed in this study were the Instron, an inertialess testing machine of the bonded strain gauge type built by the Instron Corporation, Quincy, Mass., and the Scott Serigraph Model J3, built by Scott Testers, Inc., Providence, R.I. These machines are typical of the two types in which major current interest is found. The dimensions of the specimens and the operation of either machine in conducting the tests conformed to Method 12 of the C.G.S.B. schedule dated December 31, 1952, which does not differ in any important respect from the procedures set forth by A.S.T.M. or by U.S. Federal Specification CCC-T-191b.

All results reported herein were obtained with the 55-lb. capacity range of the Scott machine, although some evidence was accumulated supporting the view that the same results would not be obtained on this machine if a different pendulum weight were used. The calibration of both machines was checked during the study. In both machines the rate of movement of the driven clamp was adjusted to 12 in./min. All specimens were conditioned in an atmosphere of 65% R.H. at 70° F. prior to testing, and the tests were carried out in the same atmosphere.

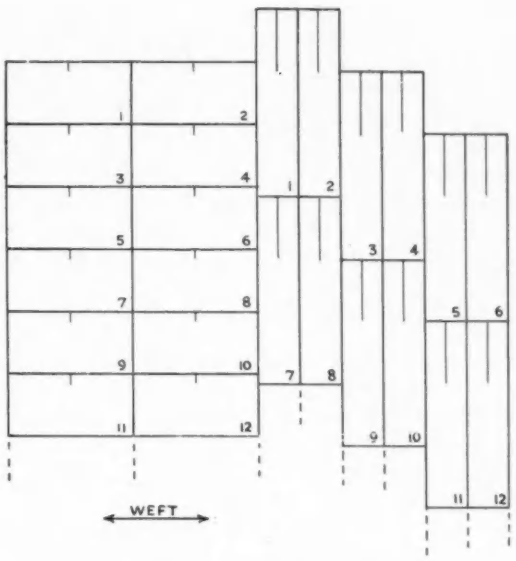

Fig. 1. Cutting pattern.

4. Results

a. Trapezoid Test

According to Millard, this type of test was originated in 1913 and was later finalized for A.S.T.M use in the form here employed. As the results of this study confirm, the data provided by this method of tearing suffer from the effect of continuously changing geometry of the stress distribution in the specimen under test. This has been recognized by others, including Kormos [3] and members of the U.S.Q.M. Research and Development Division [6]. Presumably the method was intended for the determination of tear resistance in woven fabrics in which the tearing resistances of the two sets of yarns were very different, precluding the use of the single rip test to determine the resistance of the stronger set of yarns. In any case, as will be shown, the information provided by the Trapezoid test is not easily interpreted and does not lend itself readily to analytical treatment.

Typical records obtained on the Scott and Instron

testing machines are given in Figures 2 and 3 for eight of the fabrics included in the study. Noting the several methods of interpretation listed previously, the problem of assessing each fabric in terms of an index of tearing strength is immediately apparent. In view of the fact that in some cases only a single maximum occurs in the record obtained with the pendulum-type tester, little meaning can be attached to published methods basing their interpretation on several maxima. The magnitude of the "average load necessary to tear the specimen (fabric)" is equally difficult to determine. In fact, the nature of the record obtained in many cases by the Trapezoid test on the Pendulum-type tester does not allow the treatment of data required by the standard test methods now in use.

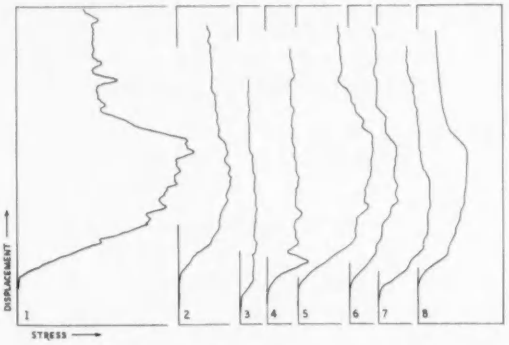

Fig. 2. Typical records, Scott tester, Trapezoid test.

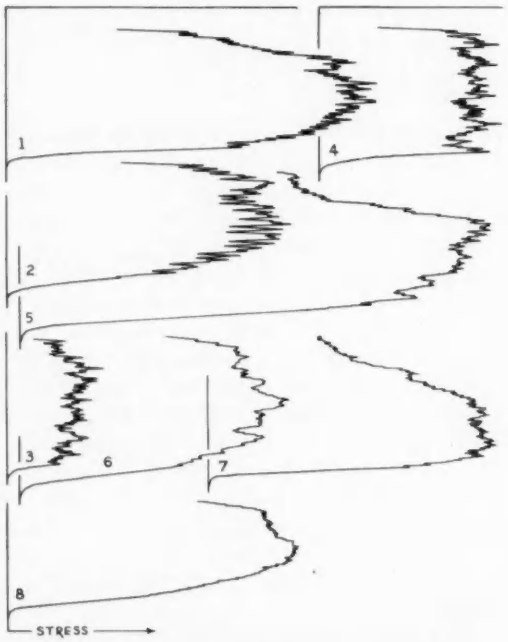

Fig. 3. Typical records, Instron tester, Trapezoid test.

The inertialess type of tensile tester provides a record of very great detail, recording as a separate maximum the breaking of individual or groups of yarns in sequence. The five highest maxima in this kind of record will differ little from the single highest maximum, as shown in Table I, in which the values of the single highest maximum, the average of the five similar highest maxima, and the average of the ten similar highest maxima are compared for the fabrics tested, average values from six specimens being given in each case.

The ratio of the average of the five highest maxima to the single highest maximum (Ratio I) is seen to have the average value 0.965, with a standard deviation of 0.016. The single (highest) maximum might therefore be taken as an index of tear strength to replace the average of the five highest maxima, without serious loss of precision, if any. Since, obviously, somewhere in every record on either machine the tearing force must reach a maximum value, whether or not other maxima appear in the curve also, this approach possesses some considerable practical merit. Creswick [1] and Garner[2] state that

TABLE I. Tearing-Strength Data (Inertialess-Type Testing Machine)

Comparison of Single Highest Maximum with Averages of Highest Five and Highest Ten Maxima Observed with the Trapezoid Method

Fabric No.	Single max. (lb.)	Average 5 max. (lb.)	Ratio I	Average 10 max. (lb.)	Ratio II
1	77.0	75.9	0.984	74.8	0.972
2	11.2	10.8	.972	10.7	.958
3	3.7	3.4	.938	3.3	.906
4	6.8	6.5	.955	6.3	.927
5	17.5	12.3	.985	17.1	.976
6	10.2	9.8	.961	9.4	.921
7	11.8	11.6	.987	11.4	.970
8	10.9	10.7	.982	10.7	.982
9	15.4	14.6	.951	13.8	.900
10	5.4	5.1	.953	5.0	.934
11	8.2	7.9	.960	7.6	.924
12	30.7	30.2	.984	30.0	.976
13	15.8	14.9	.943	14.4	.911
14	8.2	7.9	.967	7.8	.948
15	10.4	10.0	.966	9.7	.935
16	7.2	6.9	.957	6.7	.932
		Average	0.965		0.942
		Standard deviation	0.016		0.027

in the Trapezoid test the highest peak load is taken as the tear strength. While this statement is not supported by American information available to the author, it does provide a practical basis for comparing data obtained by the Trapezoid method on both pendulum and inertialess types of testing machine.

Table II presents the highest (single) maximum for each fabric (average of six specimens) by both types of testing machine.

The data of Table II are plotted in graphic form in Figure 4. It is noted that with one exception the values obtained with the Pendulum tester lie below those of the inertialess machine. The best straight line drawn through the points indicates the empirical relationship

$$(T.S.)_i = 1.13\ (T.S.)_p$$

In other words, values of tearing strength obtained on the newer type machines will average about 13% higher than those obtained with the pendulum-type tensile tester. It should be borne in mind that this comparison is based on the use of a single peak value for each specimen, it being considered that data for the Trapezoid test from the two types of testing machine are not usefully comparable on any other basis.

b. Tongue (Single Rip) Test

The principle of this method, which simulates a simple rip between two "tails," has been recognized as a standard method of test. A theoretical treatment has been published recently by Teixeira, Platt, and Hamburger [4]. The method is related to the Shirley Institute "Tongue tear test" (designated frequently as the "double tongue" method, to distinguish it from the single rip test used in Canada and the U.S.A.).

In Figures 5 and 6 are shown typical records provided by both types of testing machine for the same fabrics as represented in Figures 2 and 3. As was noted in the case of the Trapezoid test, much greater detail of the stress/time relationship in the specimen is revealed by the inertialess machine. Both machines, however, yield records similar in character and, in principle at least, amenable to the same analytical treatment.

Examination of the records reveals that for a number of fabrics a high initial peak is observed, which is not equalled by any succeeding peak. Presumably this high resistance is due to the shifting of yarns in the initial stages of the test and should not be included in the peak values used to calculate average tearing strength. It is possible that some service merit may be attached to this characteristic, in that some fabrics may resist the initiation of a tear better than others of the same average resistance to continued tearing. Whether this is so is not known, but further study may be warranted.

U.S. Federal Specification CCC-T-191b (Method 5134) requires that "the tearing strength of the specimen shall be the average of the five highest peak loads of resistance registered for 3 in. of separation of the tear." Canadian Schedule 4-GP-2

TABLE II. Comparison of Tearing Strengths (Trapezoid Method) Determined on Inertialess and Pendulum-Type Machines

Fabric	Instron (lb.)	Scott (lb.)	Ratio: Scott/ Instron
1	77.0	65.6	0.853
2	11.2	9.9	0.883
3	3.7	3.3	0.891
4	6.8	5.9	0.867
5	17.5	14.9	0.851
6	10.2	9.3	0.911
7	11.8	10.7	0.906
8	10.9	9.1	0.835
9	15.4	13.7	0.890
10	5.4	4.4	0.815
11	8.2	7.4	0.903
12	30.7	27.0	0.880
13	15.8	15.9	1.006
14	8.2	7.7	0.939
15	10.4	9.4	0.904
16	7.2	6.1	0.847
		Average	0.880
		Standard deviation	0.046

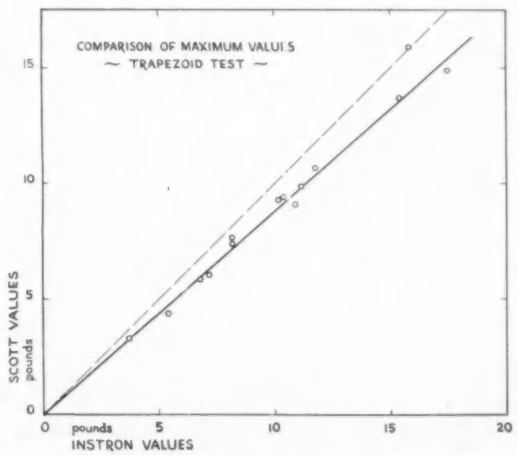

Fig. 4. Comparison of maximum values, Trapezoid test.

(Method 12) states ". . . the pull being continued until five stress maxima are obtained on the chart. The average of the five stress maxima in pounds is taken as the tearing strength of that specimen." A.S.T.M. (Committee D-13) states ". . . the average load necessary to tear the fabric shall be observed, perferably by means of an autographic recording device." While B.S.I. Handbook 11 does not list the single rip test, in connection with the "double rip" test (Shirley), it states (1949 ed., p. 141) under calculation of results, "The trace obtained consists of a series of peaks, each representing the the load at which the threads have torn, and troughs each corresponding to the fall back of the pendulum after the tear. The peaks on the charts shall be emphasized by a pencil dot and the median value of the corresponding load readings shall be found."

Of the several approaches recommended by the various standard test method references quoted above, that of the British Standards Institution was specific, appeared appropriate; and was used here noting the comment above regarding the initial peak value. The definition of a "peak" or maximum value in the record remained the same as for the Trapezoid test. Namely, a maximum is considered to be represented by any value immediately on both sides of which a lower value is recorded. Care is necessary to distinguish mere inflexions in the curve from minor maxima, and it is not entirely possible to escape a certain degree of arbitrary judgment in marking the peak values. This problem, however, is not of major proportions and does not influence the results obtained to any significant extent.

For each specimen the stress values corresponding to maxima on the record were noted, and these data for the six specimens from each fabric compiled and plotted in the form of a cumulative frequency curve. From this curve, which indicated the percentage of maxima lying below any given stress value, the median stress value or tearing strength was easily determined. In every case, the curves thus plotted exhibited a major central linear portion about the median value, reflecting an essentially normal frequency distribution of maximum stress values. In such cases, the mean or average does not differ significantly from the median. Table III presents the median values so determined.

Figure 7 illustrates these results. In every case excepting that of Fabric 8, the pendulum-type machine gave higher values than the inertialess type. The average relationship appears to be

$$(\text{T.S.})_p = 1.10\ (\text{T.S.})_i$$

i.e., the pendulum machine yields values averaging about 10% higher than the inertialess type. This fact is due probably to the appearance on the record of the latter machine of a number of small or minor peaks which are not found in the pendulum record. The pendulum machine records only the major maxima, which obviously are of a higher average

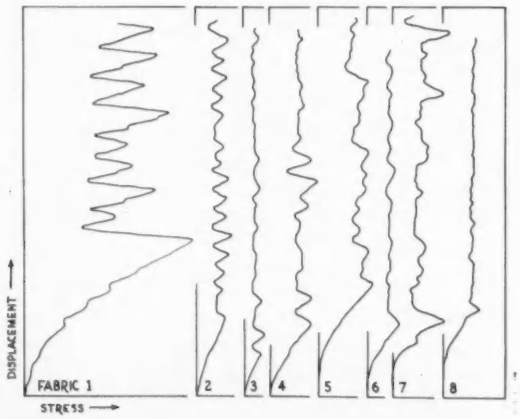

Fig. 5. Typical records, Scott tester, Tongue test.

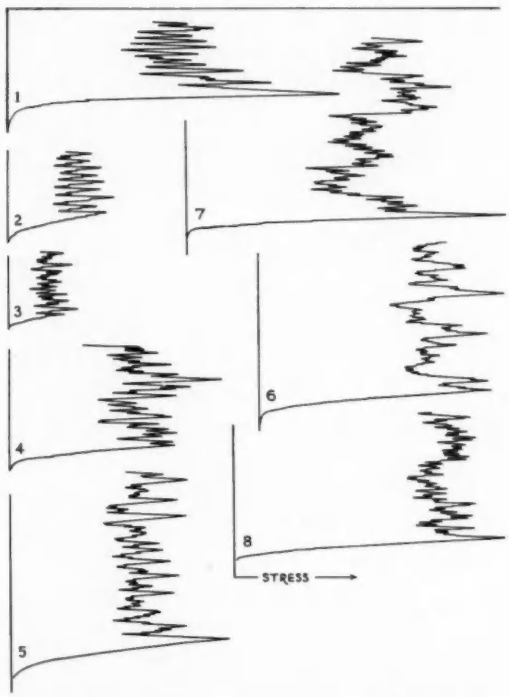

Fig. 6. Typical records, Instron tester, Tongue test.

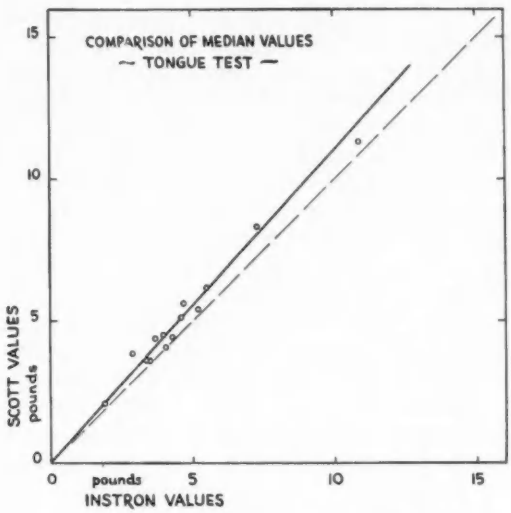

Fig. 7. Comparison of median values, Tongue test.

value. At first sight it might appear that by a selection of "major" peaks from the Instron record one could arrive at an average tearing strength value equal to that given by the present treatment of the Scott record. Undoubtedly this is so, but a major problem is encountered in defining which maxima should be recognized and which rejected in such a treatment, as reference to Figure 6 will show.

Reference has been made to cases in which the force required to initiate the tear is somewhat higher than that required to propagate it through the fabric.

TABLE III. Median Values of Tear Strength [Tongue (Single Rip) Method]

Fabric	Instron (inertialess) (lb.)	Scott (pendulum) (lb.)
1	19.5	28.0
2	2.9	3.8
3	1.9	2.1
4	5.2	5.4
5	5.5	6.2
6	3.5	3.6
7	4.0	4.5
8	4.1	4.1
9	4.3	4.4
10	3.4	3.6
11	Untearable across the weft	
12	18.5	19.4
13	10.9	11.3
14	4.7	5.6
15	7.3	8.3
16	4.6	5.1

The data obtained on the Instron machine in this study has provided the following summary of initial tearing force, averaged for six specimens of each fabric. For comparison the average force propagating the tear is also given, together with the ratio of the two values.

It is seen that quite generally the initial peak is equal to or higher than the average of succeeding peaks and should therefore as a general rule not be included in the calculation of the tearing force, defined as the average force necessary to propagate a tear through the fabric.

5. Discussion

The selection of a test method for the determination of tearing strength raises the question as to just what property it is desired to measure. It is noted (Table V) that, as reported by other authors, no general relationship exists between the values of tearing strength provided by the two test methods reviewed in this paper, and one might well ask whether either of them does in fact provide a useful index of a real aspect of service life. Viewing both methods merely as means of measurement, the Tongue (single rip) test is considerably more satisfactory than the Trapezoid method in that it provides sufficient data under stable conditions to permit the calculation of a stable

TABLE IV. Comparison of Average Tear Initiating Force and Median Value of Tearing Force

Fabric	Median value* tear force (lb.)	Average tear initiating force (lb.)	Ratio
1	19.5	30.6	1.57
2	2.9	3.8	1.31
3	1.9	2.6	1.37
4	5.2	5.6	1.08
5	5.5	8.8	1.60
6	3.5	4.5	1.29
7	4.0	7.7	1.93
8	4.1	5.2	1.27
9	4.3	4.8	1.12
10	3.4	4.1	1.20
11	—	—	—
12	18.5	25.1	1.36
13	10.9	14.3	1.31
14	4.7	7.2	1.53
15	7.3	7.3	1.00
16	4.6	4.8	1.04
		Average	1.33

* Not including initial peak force values.

TABLE V. Comparison of Tearing Strength Values Determined by the Trapezoid and Tongue (Single Rip) Methods on an Inertialess-Type Testing Machine

Fabric	Tongue Median value (lb.)	Trapezoid Average single maximum (lb.)	Ratio
1	19.5	77.0	3.95
2	2.9	11.2	3.86
3	1.9	3.7	1.95
4	5.2	6.8	1.31
5	5.5	17.5	3.14
6	3.5	10.2	2.92
7	4.0	11.8	2.95
8	4.1	10.9	2.66
9	4.3	15.4	3.58
10	3.4	5.4	1.59
11	—	8.2	—
12	18.5	30.7	1.66
13	10.9	15.8	1.45
14	4.7	8.2	1.74
15	7.3	10.4	1.42
16	4.6	7.2	1.57

index of some property of the material. From the specification aspect, this is probably sufficient to warrant its use. There remains, however, a need for further consideration of the basic problem of measurement of fabric behavior, relating to service life the ability to resist tearing under service conditions.

6. Conclusions

Currently published versions of the Trapezoid and Tongue (single rip) methods of assessment of the tearing strength of fabrics require clarification in respect to the treatment of data and calculation of the tearing strength value.

As now written, the treatment of data specified by the Trapezoid method is inadequately defined for use with pendulum-type tensile testing machines. The use of the single maximum force recorded for each specimen can be used to obtain a value as stable for practical purposes as the average value derived from several maxima and has the further advantage of application to all fabrics without equivocation. Wide variation noted between the behavior of different fabrics and between the records of the two types of tensile testing machines substantially invalidates for general use any other treatment. The method is considered less satisfactory from the statistical viewpoint than the Tongue test, the data obtained by it being considerably less in quantity per test specimen, and of much greater variability.

The Tongue (single rip) test is capable of interpretation equally well whether carried out on pendulum-type or inertialess tensile testing machines. Greater detail in the stress record and probably more reliable values are obtained with the latter. The data obtained are "well-behaved," and equally reliable values, capable of being averaged, can be obtained from a number of stress maxima for each specimen. Further study might be given to the significance (in service) of the high force required to initiate the tear in certain fabrics.

Disagreement is found between the values of tearing strength calculated for fabrics tested by inertialess and pendulum-type testing machines according to present published procedures. This is due to the inertia factor in the testing machines, and to difficulties of interpretation of the data. In the case of the Trapezoid test the calculated tearing strength (based on a single maximum per specimen) has been found to be higher when determined on the inertialess machine, averaging about 113% of the value given by the pendulum type, for the range of fabrics examined in this study. On the other hand the Tongue (single rip) method yields lower values on the inertialess machine, the average difference lying in the neighborhood of 10%.

Acknowledgment

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Literature Cited

1. Creswick, J., *J. Text. Inst.* **38**, T307 (1947).
2. Garner, W., *Textile Laboratory Manual* (2d ed.), National Trade Press, London, England (1951).
3. Kormos, P. M., *Rayon & Synthetic Textiles* **32**, 33 (1951).
4. Teixeira, N. A., Platt, M. M., and Hamburger, W. J., *Mechanics of Elastic Performance of Textile Materials: Relation of Certain Geometric Factors to the Tear Strength of Woven Fabrics*, TEXTILE RESEARCH JOURNAL **25**, 838 (1955).
5. Millard, F., *J. Text. Inst.* **38**, T419 (1947).
6. U. S. Textile Test Methods, Discussion of, prepared by Edwin B. Armstrong (O.Q.M.G.) for the Fourth Commonwealth Defence Conference on Clothing and General Stores (1953).

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Cotton Quality and Fiber Properties

Part IV. The Relation Between Single Fiber Properties and the Behavior of Bundles, Slivers, and Yarns[1]

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Abstract

The purpose of this research was to evaluate the use of single-fiber testing methods for the determination of cotton fiber properties and for the prediction of yarn quality. Samples of unprocessed cotton, finisher drawing sliver, and 36's carded yarn were obtained for 21 domestic cotton varieties representing extremes in length, fineness, and strength. Single fibers from all three processing stations were tested for their fineness and mechanical properties: crimp, Hookean slope, breaking load, elongation, elastic modulus, breaking stress, and energy to rupture. Ranges for each of these properties were established. The results were compared with the mechanical properties of the fiber bundles, slivers, and yarns.

Correlation studies of the results show that all of the mechanical properties measured on fibers are related to fiber fineness and, among the varieties, to fiber length. Bundle strengths and elongations at clamp spacings greater than 1.5 mm. relate well to fiber breaking strengths and elongations. Sliver force-extension slope is dependent on fiber fineness and fiber elastic modulus. Yarn strength depends strongly on fiber length, fineness, and elastic modulus, and only weakly on fiber strength; yarn elongation depends greatly on fiber elongation and elastic modulus.

These observations suggest that yarn strength and elongation are related to the single fiber properties and can be predicted from them fully as well as from bulk measurements of fineness and bundle strength data. They also indicate that elastic modulus is an important parameter for predicting fiber assembly behavior.

Introduction

Over 25 years ago W. Lawrence Balls [2] outlined the general relationships connecting the properties of cotton yarn with those of the raw cotton fibers. He showed that although the physical properties of the yarns depend to a considerable extent upon the properties of the constituent fibers, the relationship is not a direct one. Other factors such as yarn structure are also influential in determining yarn behavior. Many gaps in the picture showing *how* fiber properties affect the strength and elongation of yarn still remain and are the subject of attention by workers in the field.

Several approaches to the problem of *how* fibers affect yarn behavior are being employed. Platt and co-workers [12, 13] are using the analytical approach whereby mathematical expressions describing various fiber properties and their relationships to yarn properties are set up. This approach has been most successful with filament yarns. For staple yarns of fibers whose properties are not normally distributed, certain simplifying assumptions are necessary in order to apply the analytical method. The expressions thus developed are not always accurate or clear in revealing the fiber-yarn relationships sought.

Other workers [19 to 21] have used an empirical approach to the problem by statistically correlating observed cotton yarn properties with measured fiber properties for the same cotton samples. This approach does not provide a theory of how the fiber properties operate to affect yarn behavior. It does, however, permit the consideration of a larger number of fiber properties and serves as a guide for more detailed and specific studies by the analytical method.

[1] A report of work done under contract with the U.S. Department of Agriculture and authorized by the Research and Marketing Act. The contract was supervised by the Southern Regional Research Laboratory, Southern Utilization Research Branch, Agricultural Research Service.

Although in the present work similar empirical comparisons between fibers and yarns were made, the approach differs from that previously used [19 to 21] in one essential respect. In previous work the fiber data used were based on properties of the fibers in groups, bundles, or bulk. In the present work individual fibers from the samples were tested for the various parameters under consideration and the average values of these parameters employed in the statistical correlations. Comparison of the single fiber properties with the group behavior permitted an examination of the validity of the group fiber tests as indicators of fiber behavior both in and outside of the yarns. There are established herein relationships between the properties of individual cotton fibers and of yarns.

Materials

Twenty-one varieties of cotton having a wide range of fiber fineness, fiber length, and yarn strength values were selected from the 1951 crop. Table I contains a summary of the conventional fiber properties and yarn qualities for these cottons [14]. The italicized portions of the variety identifications in the table show the shortened form of cotton names which are used throughout the remainder of the paper.

The cottons were a part of the 1951 Annual Varietal and Environmental Study made by the Bureau of Plant Industry, Agricultural Research Administration. Samples of unprocessed cotton, 47-grain carded finisher drawing sliver, and 36's carded yarns were supplied to the Textile Research Institute and were processed by the Clemson Laboratory of the Cotton Branch, Production and Marketing Administration under optimum conditions for each variety [14.]

Procedures

All tests for mechanical properties were performed on the Instron Tensile Tester [9]. Room conditions were maintained at 65% relative humidity and 70° F. The properties measured and the conditions of tests are summarized in the Appendix.

TABLE I. Properties of Selected Cottons from 1951 Crop [14]

	Unprocessed cotton					36's Carded yarns
		Fibrograph length		Arealometer* fineness		Mean count-strength product
Fiber identification	Classers staple length (in.)	UHM (in.)	Mean (in.)	Surface area ($mm.^2/mm.^3$)	Shape factor D	(Skein breaks) Cotton count×lb.
Montserrat *Sea Island*	1-3/4	1.48	1.17	573	54	3299
Peruvian Tanguis	1-1/8	1.13	0.86	403	22	2159
Acala 4–42 (Shafter)	1-1/32	1.05	0.86	414	22	2556
Pima 32, Test No. 2 (Sacaton)	1-1/2	1.40	1.13	497	33	3690
Acala 44×*Pima* 32, F_1 (saw ginned) (Safford)	1-7/16	1.41	1.08	614	63	3661
A44×*P32*, F_1 ÷ *Pima 32* (50–50 mixture) (Safford)	1-1/2	1.43	1.22	543	48	3608
Acala 44×*Pima* 32, F_1 (roller ginned) (Safford)	1-1/2	1.49	1.22	575	55	3519
Mesilla Acala (State College)	1-5/32	1.18	0.90	510	34	3076
Coastland 185 (Tifton)	1-5/8	1.38	1.11	501	39	3513
Sealand 542 (Sanford)	1-5/8	1.36	1.07	534	47	3094
AHA×*Coker* 100, 50–255 (Florence)	1-3/16	1.08	0.89	395	20	2597
Triple Hybrid 458 (Statesville)	1-1/32	1.03	0.82	469	13	3884
Acala P-18C (Sacaton)	1-1/16	1.03	0.81	439	25	2202
Deltapine 15 (Stoneville)	1-3/32	1.11	0.92	406	19	2623
Watson *Mebane* (*Sacaton*)	1	0.95	0.78	385	23	1932
Watson *Mebane* # 2 (*Knoxville*)	1	0.96	0.79	402	31	1866
Empire (Experiment)	1-1/32	1.00	0.81	433	29	2434
Stormproof No. 1 (Chickasha)	13/16	0.81	0.64	538	58	1964
Stoneville 62 (Chickasha)	29/32	0.87	0.67	513	46	2206
Rowden 41B (Marianna)	31/32	1.01	0.82	357	19	2098
Delfos 7343 (Stoneville)	1-3/32	1.13	0.85	449	27	2614

* For details regarding the Arealometer measurement the reader is referred to Ref. [1].

Single Fiber Tests

Sixteen of the twenty-one available cottons were chosen for single fiber testing. Two operators, working in parallel, selected fibers at random from unprocessed cotton, finisher drawing sliver, and untwisted 36's yarns. Ten fibers of each cotton from each processing location were mounted and tested on ten different days by each operator, each processing station-cotton variety being represented each day for a total of 60 fibers of each cotton. The fibers were mounted between a brass tab and a cellulose tab by fastening with Duco cement. Details of the mounting and testing techniques have been previously reported [4, 17]. Data for computing the fiber cross-sectional area were obtained from the vibroscope attachment to the Instron [10, 11, 16, 17].

Each of the 21 cottons was examined for the number of reversals along a single fiber [16]. A structural reversal is a point in the fiber where the spiral twist of the cellulose fibrils changes from a *Z* direction to an *S* direction or vice-versa. Two observers selected 10 whole fibers at random from each of the 21 samples, mounted them on slides, immersed the fibers in oil, and counted the number of reversals in the base two-thirds, and the tip one-third, of the fiber length. A polarizing microscope with crossed nicols and a quarter-wave red plate was used for counting reversals and classifying the fiber maturity. Fibers broken in the force-extension test were examined in a similar manner and classified both as to maturity and location of break (*at* or *between* reversals).

Crimp in single fibers may be measured by three parameters, the energy E_c, the force F, or the extension E, necessary to change the fiber from its relaxed, crimped state to a straightened form [4].

The tabs, to which the fibers are cemented, are mounted for the Instron test with no initial tension on the fiber so that the fiber crimp is retained. If the initial portion of the uncrimped fiber stress-strain curve is assumed to be a straight line, then the initial curved portion of the force-extension tracing may be assumed to be caused by fiber crimp. The energy to uncrimp the fiber then is represented, on the Instron chart, by the area bounded by the extension axis, the force-extension curve and the Hookean slope line extrapolated to the extension axis. Force F, to uncrimp the fiber, is measured from the intersection of the extrapolated Hookean slope line and the extension axis. Because under the test conditions used the force-extension curve leaves the extension axis at a very slow initial rate, the starting point of extension to uncrimp the fiber is not well defined. This difficulty is avoided by measuring the extension E from a point at two-tenths of F, along a line parallel to the extension axis to the intersection with the force-extension curve.

Analysis showed that there is an approximate linear relation between the uncrimping force and extension on the one hand, and the uncrimping energy on the other. All three parameters change in the same manner with processing so that any one of the three may be used to characterize the crimp. The uncrimping energy was used in this test.

Flat Bundle Tests

Flat bundle tests on all 21 cottons were performed by one operator on a schedule designed to eliminate day and clamp effects with Empire and Sak cottons as controls. The Instron machine was fitted with holders [15] for Pressley clamps at nominal gauge lengths of 0.0, 1.5, and 5.0 mm. In order to have about the same rate of extension at each spacing, crosshead speeds were set at 0.1, 0.2, and 0.5 in./min., respectively. Eight tests were made on each cotton at each spacing.

Tests on 47-Grain Finisher Drawing Sliver

Eighteen-inch specimens were cut and weighed in order to determine sliver size. No sliver was discarded between samples. Each sample was tested with special clamps on the Instron machine at a clamp spacing of 10 in. The initial slope and maximum load supported by the sliver before beginning to pull apart were measured from the force-extension curves. The initial slope and the maximum load were normalized to a unit weight basis to eliminate small differences in sliver size. Five tests were made on each cotton on each of three days for a total of fifteen tests per cotton.

36's Carded Yarns

Yarn strengths and elongations were determined for each of the carded yarns at gauge lengths of 2 and 20 in. A total of 60 breaks was made for each cotton at each spacing.

Data Processing

All test data were transcribed from the charts and punched into IBM cards. Calculation of mean values, variances, and coefficients of variation was performed on the type 602-A Calculating Punch.

Card handling was facilitated by the use of other standard IBM equipment. Special control panels were wired to make the correlation calculations and some of the analyses.

Results

Single-Fiber Mechanical Properties

Effects of processing. Mean values of the single fiber properties for each variety are shown in Table II. The forces imposed on the single fibers during processing cause changes in some fiber properties. The mean Hookean slope of fibers drawn from yarn was 21% greater than the mean slope of fibers from the finisher drawing sliver with a corresponding increase in the elastic modulus. Fiber elongation to break increased 6% from the unprocessed cotton to the sliver and decreased 8% from the sliver to the yarn. The energy to uncrimp decreased 38% from ginned

TABLE II. Mean Values of Single Fiber Properties by Varieties

Fiber identification	Cross-sectional area ($cm.^2 \times 10^{-6}$)	Uncrimping energy (g. cm./cm. $\times 10^{-3}$)			Elongation to break (%)			Breaking load (g.)	Breaking stress [$(g./cm.^2) \times 10^6$]
		Bale	Sliver	Yarn	Bale	Sliver	Yarn		
Sea Island	1.02*	0.90†	0.87†	0.55†	7.9†	10.7†	8.9†	5.75*	5.25*
Peruvian Tanguis	1.35	1.74	1.07	0.71	8.1	9.7	9.1	5.65	4.25
Acala 4–42	1.36	2.49	1.40	1.02	6.6	7.4	5.7	5.10	3.88
Pima 32	1.00	1.44	1.31	0.67	7.5	7.9	7.9	5.69	5.31
Acala×Pima (rg)	0.93	0.83	0.49	0.49	9.5	10.6	9.6	5.21	5.34
Coastland	0.98	0.94	0.95	0.75	6.4	8.1	7.4	5.58	5.44
Sealand	1.03	2.37	0.89	0.57	7.2	6.9	6.2	4.42	4.37
Triple Hybrid	0.95	2.15	1.25	0.91	5.5	5.5	5.4	5.55	5.14
Acala P-18C	1.26	1.60	1.00	0.70	10.5	10.7	9.1	4.38	3.48
Deltapine	1.42	2.41	1.53	1.15	8.9	8.0	7.6	6.10	4.49
Mebane (Sacaton)	1.61	2.16	1.40	1.11	12.9	12.2	10.4	6.02	3.86
Empire	1.36	2.36	1.08	1.04	6.6	7.7	6.8	5.42	4.08
Stormproof	1.18	2.15	1.42	0.76	6.6	6.2	6.3	4.13	3.57
Stoneville	1.31	2.85	1.48	1.15	5.8	6.4	7.3	4.40	3.45
Rowden	1.66	2.39	1.84	1.36	7.9	7.9	7.6	6.87	4.01
Delfos	1.21	1.73	0.90	0.80	8.9	8.9	8.2	4.54	3.88
Average	1.23	1.91	1.18	0.86	7.9	8.4	7.7	5.30	4.36

Fiber identification	Hookean slope (g./%)			Elastic modulus ($g./cm.^2/\% \times 10^6$)			Energy to break (g. cm./cm. $\times 10^{-3}$)	% Breaking at reversals	No. reversals per cm. of fibers
	Bale	Sliver	Yarn	Bale	Sliver	Yarn			
Sea Island	0.86†	0.67†	0.80†	0.93†	0.66†	0.88†	267*	47*	24.5*
Peruvian Tanguis	0.72	0.70	0.87	0.56	0.54	0.69	279	57	22.6
Acala 4–42	0.71	0.79	1.02	0.54	0.60	0.76	181	35	20.8
Pima 32	0.87	0.79	0.87	0.91	0.79	0.98	227	40	16.9
Acala×Pima (rg)	0.62	0.66	0.73	0.62	0.76	0.85	253	52	27.4
Coastland	0.86	0.84	0.98	0.91	0.82	1.20	211	53	18.3
Sealand	0.70	0.79	0.79	0.60	0.75	0.91	165	32	18.7
Triple Hybrid	0.86	0.80	1.22	0.84	0.89	1.32	153	32	16.8
Acala P-18C	0.51	0.55	0.68	0.42	0.43	0.60	227	47	26.8
Deltapine	0.71	0.72	1.04	0.53	0.55	0.76	255	52	21.1
Mebane (Sacaton)	0.57	0.70	0.73	0.33	0.51	0.50	354	50	21.2
Empire	0.89	0.88	0.87	0.62	0.69	0.73	204	37	27.9
Stormproof	0.63	0.69	0.86	0.54	0.59	0.73	143	40	27.8
Stoneville	0.73	0.63	0.86	0.58	0.49	0.67	154	40	26.9
Rowden	0.88	0.98	1.17	0.52	0.62	0.87	278	38	21.6
Delfos	0.63	0.68	0.84	0.55	0.55	0.76	210	50	22.3
Average	0.73	0.74	0.89	0.62	0.64	0.82	223	44	22.6

* Means based on 60 fibers selected from all processing stations tested.
† Means based on 20 fibers taken from processing station indicated.

TABLE III. Correlation of Individual Fiber Properties Within Each Cotton

x Value	Area			Breaking load		Breaking elongation		
y Value	Breaking load	Uncrimping energy	Elastic modulus	Breaking elongation	Hookean slope	Hookean slope	Elastic modulus	Breaking stress
Sea Island	0.525	0.320	−0.529	0.432	0.384	−0.393	−0.630	0.018
Peruvian Tanguis	0.465	0.338	−0.395	0.618	0.526	−0.156	−0.364	0.381
Acala 4–42	0.167	0.645	−0.222	0.613	0.393	−0.347	−0.303	0.613
Pima 32	0.468	0.350	−0.345	0.614	0.439	−0.307	−0.457	0.447
Acala × Pima (rg)	0.452	0.562	−0.223	0.527	0.462	−0.257	−0.333	0.593
Coastland	0.322	0.173	−0.416	0.585	0.359	−0.391	−0.345	0.554
Sealand	0.509	0.344	−0.154	0.336	0.590	−0.357	−0.364	0.424
Triple Hybrid	0.550	0.237	−0.070	0.400	0.682	−0.206	−0.296	0.459
Acala P-18C	0.501	0.535	−0.319	0.519	0.382	−0.377	−0.422	0.480
Deltapine	0.217	0.658	−0.401	0.624	0.342	−0.317	−0.166	0.665
Mebane	0.419	0.454	−0.379	0.537	0.283	−0.305	−0.147	0.664
Empire	0.498	0.648	−0.414	0.432	0.470	−0.252	−0.099	0.547
Stormproof	0.449	0.464	−0.018	0.454	0.586	−0.228	−0.094	0.683
Stoneville	0.269	0.397	−0.268	0.476	0.383	−0.329	−0.342	0.464
Rowden	0.026	0.182	−0.433	0.519	0.473	−0.300	−0.206	0.668
Delfos	0.204	0.461	−0.330	0.363	0.519	−0.368	−0.344	0.301

With 58 degrees of freedom a value greater than 0.250 is needed for statistical significance at the 5% level.

cotton to the sliver, and 55% from unprocessed cotton to yarn. No changes in other fiber properties were observed. Processing effects are also shown in Table II.

Correlation of fiber properties within each variety. Correlation coefficients between all fiber properties were calculated for the fibers of each variety of cotton. For most varieties there is a positive correlation between fiber cross-sectional area and the uncrimping energy. Fiber area also correlates positively with the breaking load and negatively with the elastic modulus. For all cottons there is a positive correlation between fiber breaking load and the elongation to break and the Hookean slope. Fiber elongation to break is correlated negatively with Hookean slope and elastic modulus and positively with the breaking stress. Those coefficients which are significant are summarized in Table III.

Because of the changes in some fiber properties with processing, as described above, the correlations were made at two levels; the first included only those fibers from the unprocessed cotton and the second included fibers from all processing locations. Coefficients obtained from the second group were somewhat higher than for the first group. It is likely that this is due to a larger number of fibers (60 per cotton) being included, although processing effects which tend to lower the correlations are also involved.

TABLE IV. Correlation of Mean Values of Fiber Properties between Sixteen Cotton Varieties

x Property	*y* Property	For mean values of fibers from: Unprocessed cotton	Yarn
Area of cross section	Uncrimping energy	0.643	0.766
	Elastic modulus	−0.765	−0.707
	Breaking stress	−0.519	−0.684
	Mean length	−0.562	−0.653
Breaking load	Hookean slope	0.376	0.743
Elongation to break	Hookean slope	−0.634	−0.621
	Elastic modulus	−0.571	−0.495
Uncrimping energy	Elastic modulus	−0.520	−0.217
	Breaking stress	−0.614	−0.474
	Mean length	−0.714	−0.640
Elastic modulus	Breaking stress	−0.656	−0.730
	Mean length	−0.607	−0.445
Breaking stress	Mean length	0.659	0.839

With 14 degrees of freedom a value of 0.497 is necessary for statistical significance at the 5% level.

Correlation of fiber properties between varieties.[2] Correlation coefficients between all fiber properties were calculated using the mean values for each cotton. Significant correlations are shown in Table IV.

[2] Strictly speaking the values correlated herein should be for a random sample from a normal bivariate population. In a study such as this some departure from a purely random sample is unavoidable. All cottons are not available at the same time for sampling, and the use of a finite gauge length in fiber testing requires selection of only those fibers of at least that length. The authors recognize that such selection will have the effect of lowering the significance levels of correlations somewhat.

For the most part the correlations between and within varieties have the same relations. Exceptions to this involve the breaking load or the breaking stress. It should also be noted that the coarse varieties are weaker in strength per unit area than the fine cottons (see Figure 1).

Correlation calculations were made at two levels: between means for the fibers from the unprocessed cotton and between means for the fibers from the yarn. This division showed some differences in the correlation coefficients obtained when one or both of the properties had been modified by processing. For example, the uncrimping energy and the elastic modulus, each of which was modified by processing, are correlated with a coefficient of 0.520 (negative) when the fibers from unprocessed cotton are considered, but with a coefficient of only 0.217 (negative) when the mean values of the fibers from yarn are used. The latter value is not statistically significant at the 5% level with 14 degrees of freedom.

To examine the relations more closely, the data cards for all fibers, regardless of variety, were arranged in order of fiber fineness and arbitrarily divided into 16 groups. The mean values of the fiber properties for each of these groups were found, and the results are shown plotted in Figure 2. When arranged in this manner, the fiber crimp and elastic modulus show strong dependence on the fiber fineness.

Flat Bundle Tests

Effects of gauge length. Results of the flat bundle tests are shown in Table V. The initial spacing

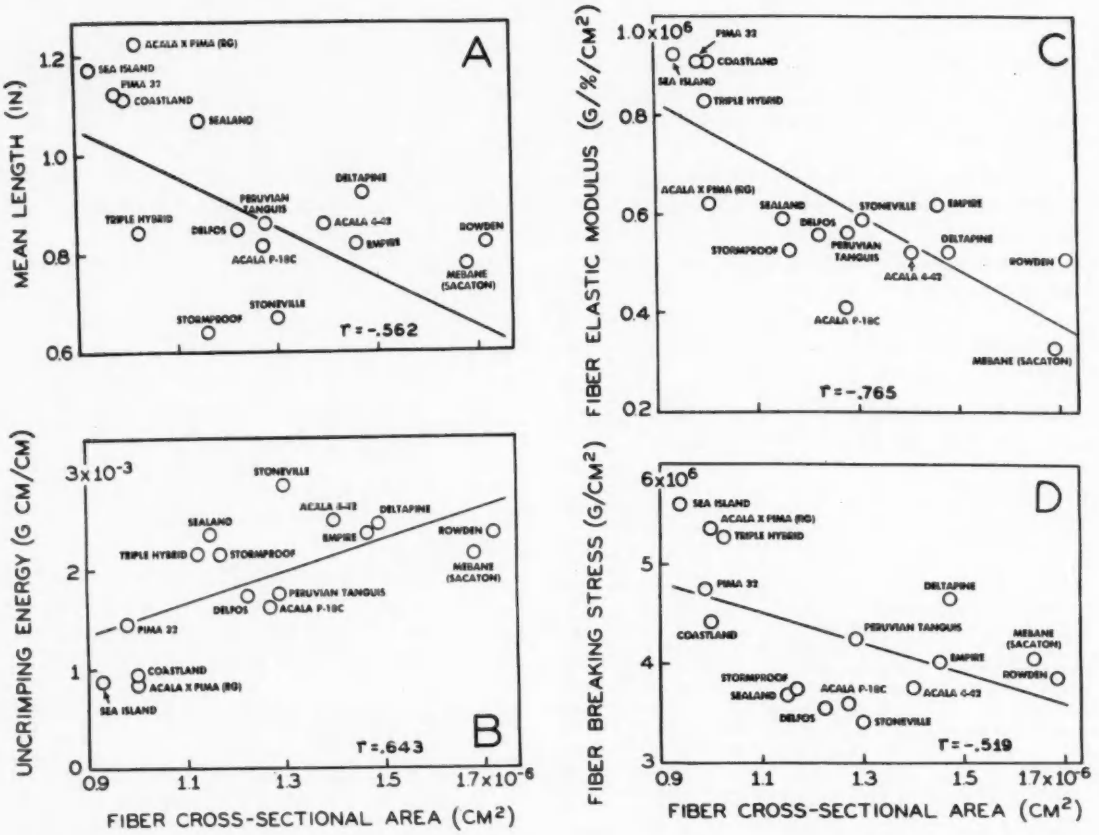

Fig. 1. Relation between average fiber cross-sectional area and average values of (A) mean length, (B) uncrimping energy, (C) elastic modulus, and (D) breaking stress for unprocessed fibers of different varieties of cotton.

between Pressley clamps in a bundle test has a marked effect on the strength and elongation of the bundle, an increase in spacing resulting in decreased values for those two properties. These losses are not the same for all cottons.

Since fiber reversals have been shown to be weak places in the fiber [16], it was not surprising to find that cottons having the largest number of reversals per unit length (shown in Table II) made weaker bundles. (Cottons which were found to deviate from this relationship are Mesilla Acala, which was stronger than expected, and Watson Mebane, which was weaker.) The number of fiber reversals, however, appears to have no effect on the strength lost as the clamp spacing is increased (Table VI).

Correlation of single fiber and bundle tests. The mean fiber breaking stress for each cotton correlates well with bundle strength, normalized on a weight basis; and mean fiber elongations correlate strongly with bundle elongations. The correlations are better at the longer gauge lengths (Table VI and Figure 3). Other fiber properties are also related to the bundle properties, but since these fiber properties are interrelated, such correlations are expected.

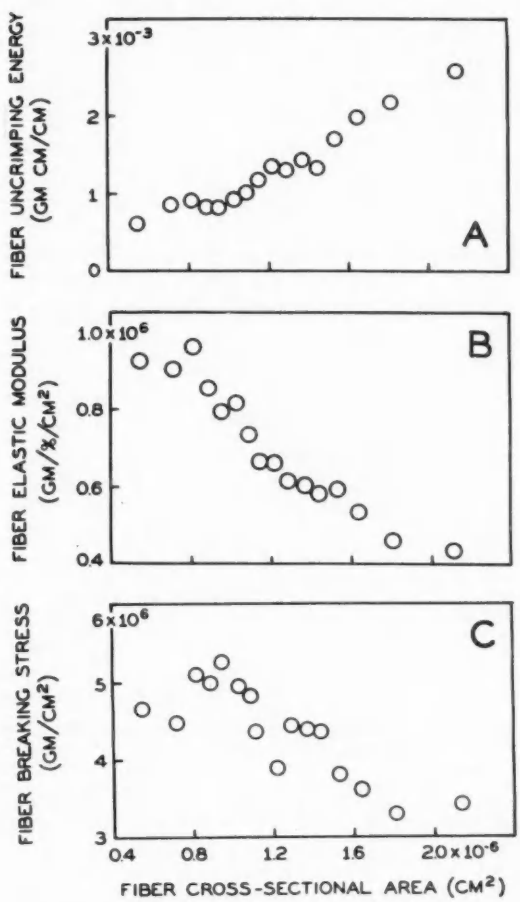

Fig. 2. Relation of average fiber cross-sectional area to average values of (A) uncrimping energy, (B) elastic modulus, and (C) breaking stress for fibers of all varieties studied.

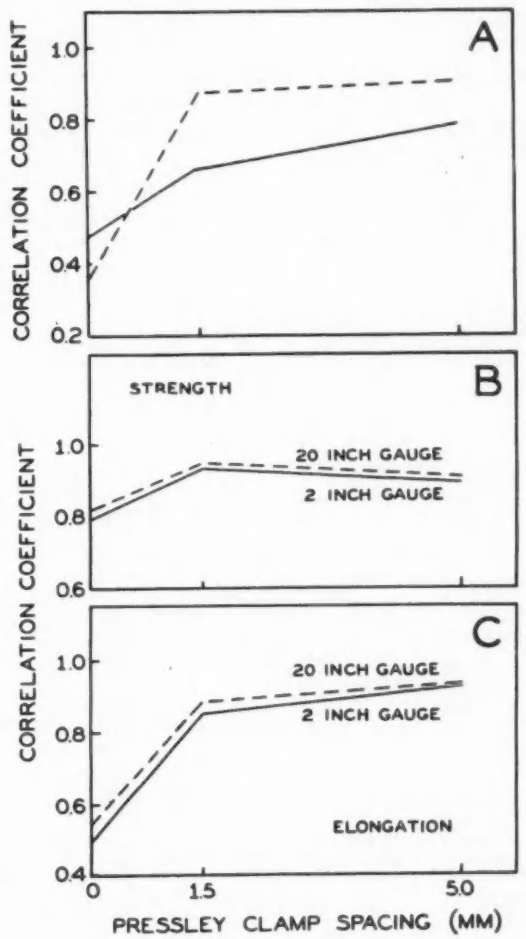

Fig. 3. Effect of Pressley clamp spacing on the correlations between (A) fiber and bundle strengths (solid line) and fiber and bundle elongations (dotted line), (B) bundle and yarn strengths, (C) bundle and yarn elongations. Bundle tests were made using unprocessed cotton.

TABLE V. Properties of Fiber Assemblies

Cotton	Flat bundles (unprocessed cotton)						Finisher drawing sliver 47 Grain			36's Carded yarns single end	
	Strength (g./grex)			Elong. at max. load* (%)			Weight (grains)	Max. load (g.)	Slope (g./%)	Load (g.)	Elongation (%)
	0 mm.	1.5 mm.	5.0 mm.	0 mm.	1.5 mm.	5.0 mm.					
Sea Island	4.00	2.64	2.04	13.0	8.9	7.3	46.2	36.9	8.4	337	8.6
Peruvian Tanguis	3.83	2.40	1.70	12.7	9.7	8.5	48.4	39.8	7.3	216	8.5
Acala 4–42	4.11	2.50	1.59	13.2	7.4	6.1	47.6	50.0	9.5	269	7.3
Pima 32	4.80	3.42	2.53	15.5	8.1	6.8	48.7	56.3	12.2	389	7.8
Acala×Pima (sg)	4.50	3.26	2.43	15.0	10.8	8.8	47.3	40.6	10.4	366	9.0
A44×P32–P32	4.41	3.18	2.46	15.4	10.5	7.8	47.4	46.4	11.1	380	8.4
Acala×Pima (rg)	4.09	3.15	2.33	15.5	10.9	9.1	46.1	39.8	10.0	362	9.1
Mesilla Acala	3.98	2.74	1.95	16.2	9.5	8.2	47.1	53.8	11.0	314	8.7
Coastland	4.68	3.37	2.25	14.1	7.8	6.3	47.7	50.7	11.3	363	7.7
Sealand	4.18	2.63	1.59	14.8	7.8	6.3	45.2	42.2	10.4	329	7.6
AHA×Coker	4.20	2.85	1.80	13.9	8.2	5.6	46.7	35.4	7.3	284	6.6
Triple Hybrid	5.48	3.58	2.14	14.9	8.0	6.1	49.3	62.6	12.1	396	6.9
Acala P-18C	3.45	2.20	1.55	16.2	11.8	10.5	47.9	51.2	9.9	236	9.7
Deltapine	4.08	2.61	1.99	15.5	8.9	7.5	47.2	51.5	9.5	254	7.9
Mebane (Sacaton)	3.01	1.75	1.30	13.5	11.0	9.6	47.5	52.7	8.2	207	10.1
Mebane (Knoxville)	3.06	1.83	1.31	19.2	11.1	9.3	47.5	38.1	7.3	209	9.5
Empire	3.85	2.32	1.53	13.2	8.0	6.5	48.6	44.7	7.3	275	8.1
Stormproof	3.80	1.88	1.16	15.1	6.7	5.9	48.7	46.5	7.9	218	7.9
Stoneville	4.06	2.12	1.28	11.5	7.0	5.5	47.6	41.8	7.3	221	7.2
Rowden	4.09	2.37	1.56	13.9	6.8	6.8	46.3	43.1	8.1	222	7.5
Delfos	3.89	2.46	2.38	14.4	9.9	7.6	47.7	46.4	9.0	267	8.5

* Elongations are based on the extension to maximum force and the assumption of an actual gauge length of 1 mm. for the zero clamp spacing.

TABLE VI. Correlation of Single Fiber and Assembly Properties

Fiber property	Flat bundles						Finisher drawing sliver				36's Carded yarns			
	Bundle strength			Bundle elongation			Maximum load		Slope		Breaking load		Elongation	
	Fibers from unprocessed cotton only						Fibers from		Fibers from		Fibers from		Fibers from	
	Clamp spacing (mm.)			Clamp spacing (mm.)			Unprocessed cotton	Sliver	Unprocessed cotton	Sliver	Unprocessed cotton	Yarn	Unprocessed cotton	Yarn
	0.0	1.5	5.0	0.0	1.5	5.0								
Area of cross section	−0.573	−0.663	−0.632	−0.133	0.175	0.184	−0.127	−0.269	−0.562	−0.680	−0.763	−0.856	−0.102	0.188
Breaking load	0.032	0.073	0.260	0.230	0.243	0.233	0.115	−0.210	0.084	0.000	0.022	0.123	0.126	−0.337
Elongation to break	−0.703	−0.388	−0.129	0.353	0.870	0.897	−0.169	−0.411	−0.141	−0.226	−0.337	−0.223	0.868	0.863
Hookean slope	0.653	0.525	0.453	−0.032	−0.557	−0.634	0.152	0.148	0.182	0.113	0.112	0.161	−0.641	−0.769
Uncrimping energy	−0.116	−0.486	−0.680	−0.325	−0.418	−0.397	0.123	0.278	−0.360	−0.227	−0.541	−0.527	−0.478	−0.344
Elastic mod.	0.770	0.792	0.760	0.104	0.409	0.460	0.215	0.342	0.535	0.681	−0.303	−0.150	0.608	0.466
Break. stress	0.475	0.666	0.785	0.316	0.119	0.079	0.102	−0.238	0.408	−0.191	0.699	0.828	−0.407	−0.581
Energy to break	0.549	0.312	0.052	0.244	0.644	0.670	−0.139	−0.426	−0.229	−0.240	0.827	0.826	0.035	−0.216
Mean length							−0.105		0.138		0.745		0.115	
Reversal freq. in base ⅜ of fiber	−0.445	−0.435												

With 14 degrees of freedom a value of 0.497 is needed for statistical significance at the 5% level and a value of 0.623 for significance at the 1% level.

Mechanical Properties of 47-Grain Finisher Drawing Sliver

Large differences between cottons were found for the two sliver properties measured, maximum load and the slope of the force-extension curve. Part of these differences could be attributed to small differences in sliver weight (Table V).

These tests, which were performed over a period of three days, showed a pronounced day effect which could not be attributed to conditioning of the samples. The force to break and the initial slope of the force-extension curve increased through the three days of testing, while the weight of the sliver decreased. Analysis of the data showed a significant difference between the cottons in their response to this day effect; they were not affected equally. It may be that these variations are due to differences along the sliver. These data demonstrate that it is necessary to make a sufficient number of tests and to take samples from separated places along the length of the sliver in order to obtain reliable mean values.

Correlations of single fiber and bundle properties with finisher drawing sliver behavior. The maximum load which the sliver will bear before the fibers begin to slip apart is not related to any of the fiber properties measured in this test (Table VI). This observation suggests that the arrangement of the fibers in the sliver is more important to the sliver strength than the fiber properties themselves.

The fineness of fibers drawn from sliver is correlated negatively with the sliver slope with a coefficient of 0.680 (Table VI). This relation probably accounts for the correlation of fiber elastic modulus with the sliver slope since this fiber property is related to the fiber fineness.

The slope of the sliver curve is also related to the Pressley bundle strength (Table VII).

36's Carded Yarns

Mean strengths and elongations for each of the 21 cottons are shown in Table V.

Correlation of yarn and flat bundle strengths and elongations. Correlation of the data from flat bundle tests was made with yarn strengths and elongations for each bundle jaw spacing and each gauge length of the yarn tests. Correlation coefficients close to unity were found between bundle and yarn strengths and elongations. The best predictions of yarn behavior are made when the higher flat bundle jaw spacings are used. In all cases the correlations of bundle properties with the yarn properties at the 20-in. yarn gauge length were slightly better than with the 2-in. yarn gauge length results (Figure 3).

Correlation of fiber and yarn properties. Single-fiber mean values for each cotton were correlated with yarn strengths and elongations at each yarn gauge length (Table VI). Coefficients for the two gauge lengths are nearly the same in all cases. Separate coefficients were calculated for the fibers from the ginned cotton and for the fibers from the yarns. In most cases the coefficients are somewhat higher for the fibers drawn from the yarns, but the differences are small.

The yarn strength is related to five fiber properties: fineness, uncrimping energy, elastic modulus, breaking stress, and mean length (Figure 4). Strong yarns result from fine fibers with small crimp and high values of modulus, strength, and length.

Fiber elongation is the most important fiber property influencing yarn elongation. As with yarn strength, yarn elongation is increased by having fibers with small crimp, but the elastic modulus acts in the opposite manner; that is, high values of elongation are associated with low values of elastic modulus (Figure 5). Better correlation is found between the actual fiber stiffness (Hookean slope line) and the yarn elongation than between the stiffness per unit area (elastic modulus).

Since, as has been shown previously, some of the fiber properties are interrelated, the apparent effects of any one fiber property may include the effects of others as well. The relative importance of each, when the others are held constant, was therefore studied by the use of multiple correlation methods.

The five fiber properties related to the yarn strength are area of cross section, uncrimping en-

TABLE VII. Correlation of Finisher Drawing Sliver with Pressley Bundle Properties

		Correlation coefficients	
	Pressley gauge (mm.)	Pressley strength	Pressley elongation
Sliver strength	0.0	0.472	0.170
	1.5	0.358	−0.143
	5.0	0.248	−0.095
Sliver initial slope	0.0	0.677	0.307
	1.5	0.714	0.085
	5.0	0.703	0.025

A value of 0.433 (degrees of freedom = 19) is needed for statistical significance at the 5% level.

ergy, breaking stress, elastic modulus, and mean length. If the uncrimping energy, which is strongly dependent on the fineness, is corrected for the fineness by dividing the former by the latter, the resulting parameter has no relation to the yarn strength, showing that the apparent correlation of fiber crimp and yarn strength is actually an area correlation.

For this reason only the remaining four fiber properties were used as independent variables in the multiple correlation with yarn strength. The regression equation derived was

$$Y=147\times10^{-6}X_1-1\times10^{-6}X_2-90\times10^{6}X_3+132X_4+156 \quad (1)$$

where

Y	yarn strength	g.
X_1	elastic modulus	$\times10^{6}$ g./%/cm.^{2}
X_2	breaking stress	$\times10^{6}$ g./cm.^{2}
X_3	area of cross section	$\times10^{-6}$ cm.^{2}
X_4	mean length	in.

The multiple correlation coefficient associated with this equation is 0.946 and the standard error of estimate is 21.5. Because the breaking stress has a small partial correlation coefficient and a small effect on yarn strength (Table VIII), a second equation in which the breaking stress was eliminated as a variable was also derived.

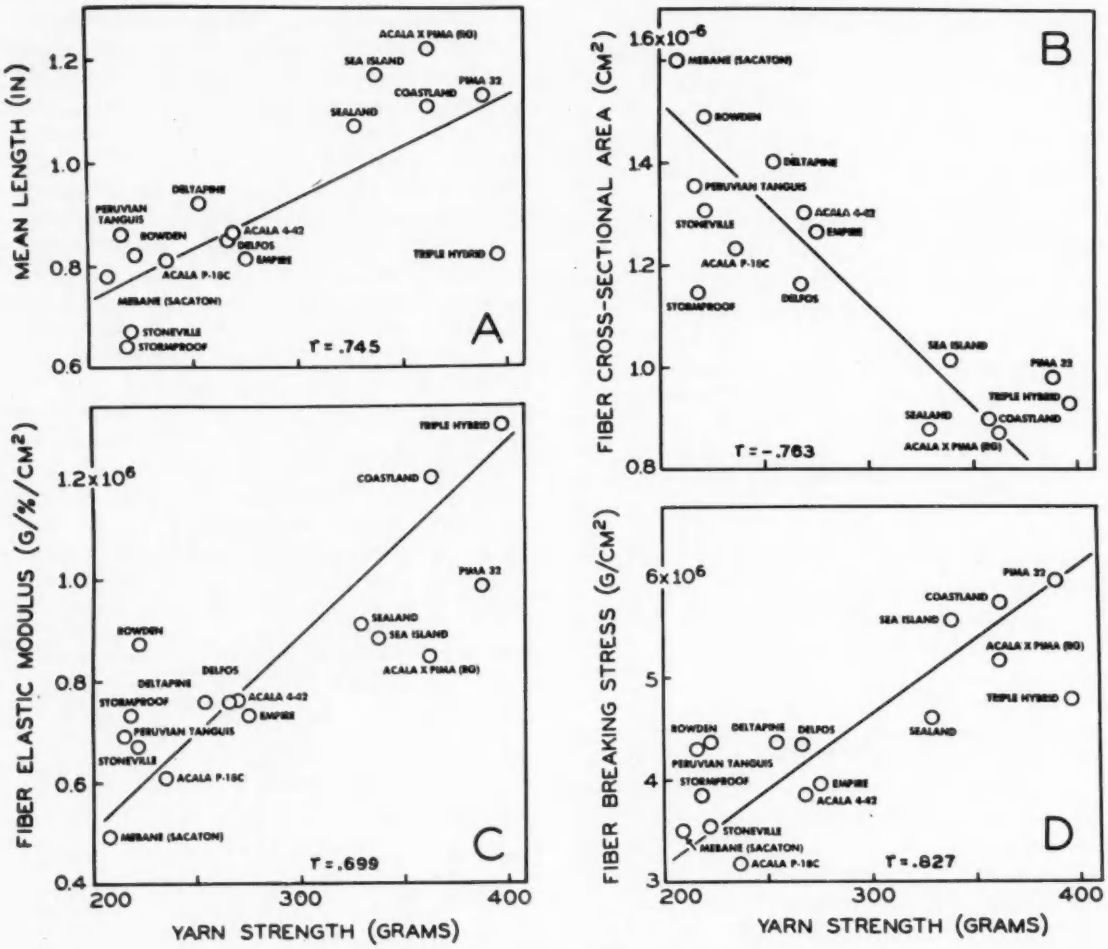

Fig. 4. Effect on single end yarn strength of (A) fiber mean length, (B) cross-sectional area, (C) elastic modulus, and (D) breaking stress for different varieties. Single fiber values are for fibers from yarn.

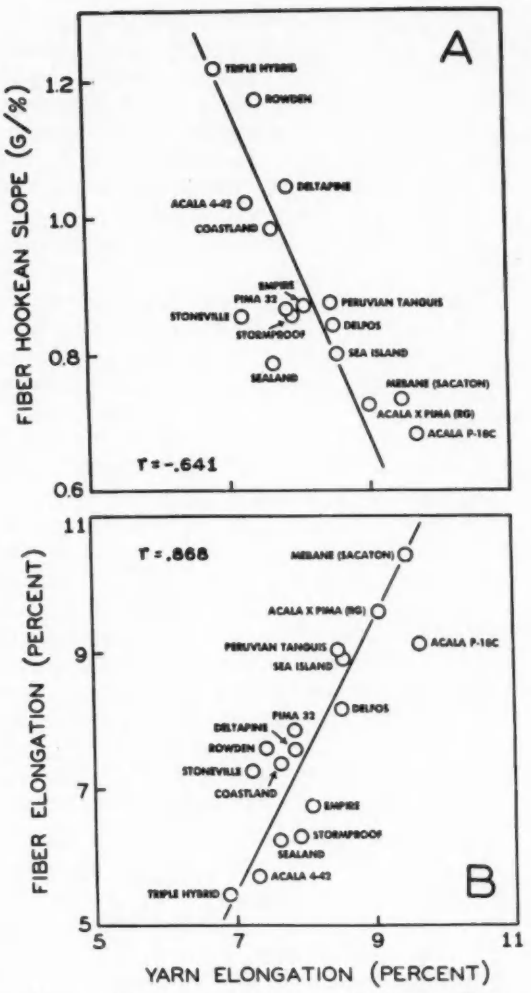

Fig. 5. Effect on yarn elongation of (A) fiber Hookean slope and (B) fiber breaking elongation for different cotton varieties. Single fiber values are for unprocessed cotton.

$$Y = 144 \times 10^{-6} X_1 - 91 \times 10^{6} X_3 + 127 X_4 + 157 \quad (2)$$

This equation has an associated correlation coefficient of 0.946 and a standard error of estimate of 21.5. The partial correlation coefficients associated with each of the variables and the effect that each variable can have on the yarn strength when minimum and maximum values are inserted in the equations are shown in Table VIII. Figure 6 is a plot of the yarn strengths calculated from this equation against the measured yarn strengths.

In a similar manner Equation 3 for the breaking elongation of yarns was derived. Here the crimp per unit area was included since it was found to be related to the yarn elongation with a simple correlation coefficient of -0.627.

$$Y = -0.712 \times 10^{-6} X_1 - 0.836 \times 10^{-3} X_5 + 0.428 X_6 + 5.991 \quad (3)$$

where X_1 is the elastic modulus as before, X_5 is the crimp energy per unit area, and X_6 is the fiber elongation to break. The small value of the partial coefficient for the crimp per unit area led to the derivation of another equation in which this parameter was not considered (Table VIII).

$$Y = -0.808 \times 10^{-6} X_1 + 0.473 X_6 + 5.133 \quad (4)$$

These equations have multiple correlation coefficients of 0.888 and 0.867, respectively, and standard errors of estimate of 0.38 and 0.41, respectively. Figure 7 is a plot of the yarn elongations calculated from this equation against the measured yarn elongations.

Discussion and Conclusions

The results of these tests show that the mechanical properties of cotton single fibers can be used to dis-

TABLE VIII. Multiple Correlation of Single Fiber Properties with Yarn Strength and Elongation

Fiber property	Effect on yarn	Partial correlation coefficients
	Equation 1	
X_1	73.2 to 194.6 g.	0.581
X_2	− 4.3 to − 8.0	−0.018
X_3	−79.3 to −146.0	−0.496
X_4	84.5 to 161.0	0.420
	Equation 2	
X_1	71.8 to 190.9 g.	0.703
X_3	−79.8 to −147.0	−0.522
X_4	81.6 to 155.0	0.621
	Equation 3	
X_1	−0.35 to −0.94%	−0.316
X_5	−0.42 to −0.83	0.239
X_6	2.33 to 4.47	0.752
	Equation 4	
X_1	0.40 to 1.07%	−0.503
X_6	2.57 to 4.94	0.785

Fiber property and range of mean values

X_1 Elastic modulus (0.496 to 1.318) $\times 10^6$ g./%/cm.^{2}
X_2 Breaking stress (0.318 to 5.97) $\times 10^6$ g./cm.^{2}
X_3 Area of cross section (0.876 to 1.614) $\times 10^{-6}$ cm.^{2}
X_4 Mean length (0.64 to 1.22) in.
X_5 Crimp per unit area (0.505 to 0.990) $\times 10^3$ g./cm.^{2}
X_6 Elongation to break (5.44 to 10.44) %

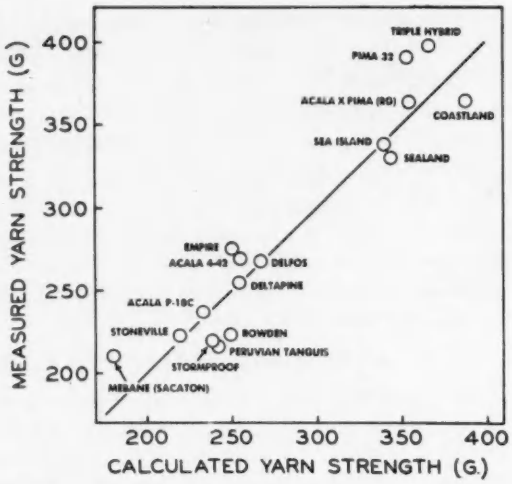

Fig. 6. Multiple correlation of single fiber properties with yarn strength. The line shown is for 1:1 ratio of measured to calculated strength (Eq. 2).

tinguish between varieties, and that varietal differences in slivers and yarns can be traced to the differences between the average property values for the single fibers of which they are made.

Most previous work in relating fiber and yarn properties has involved the properties of groups of fibers such as Pressley bundles from which the strength and elongation of yarn can be closely approximated. The closeness of this relationship between Pressley bundle properties and yarn behavior, although very useful as a practical relationship employed by mill laboratories, is at the same time a misleading one. Measurements on the bundle only roughly indicate fiber properties, and much more precisely indicate yarn properties because the bundle is in reality a yarnlike fiber assembly.

Several difficulties are encountered in the use of bundle measurements to evaluate fiber properties. The gauge length used in the bundle tests influences the values obtained, lower values resulting from increases in jaw spacing. Furthermore, the decreases in strength and elongation are not proportional for all cottons. It has already been shown that the magnitude of the strength decrease is not related to the frequency of weak places found along the length of the cotton fiber. There appears to be some other fiber property, or properties, differing between cottons, which may be related to this bundle behavior. The results shown in Figure 8 indicate that fiber crimp is such a property. Possibly crimp in the fiber makes more difficult the formation of a good bundle in which all the fibers are parallel with equal lengths and tensions between the clamps. In such a situation the full potential strength of the fibers is not realized. This crimp effect becomes more pronounced at longer gauge lengths, giving rise to the greater strength decreases indicated in Table V.

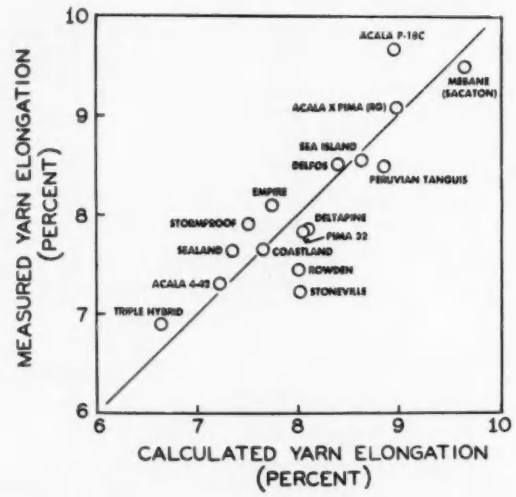

Fig. 7. Multiple correlation of single fiber properties with yarn elongation. The line shown is for 1:1 ratio of measured to calculated elongation (Eq. 4).

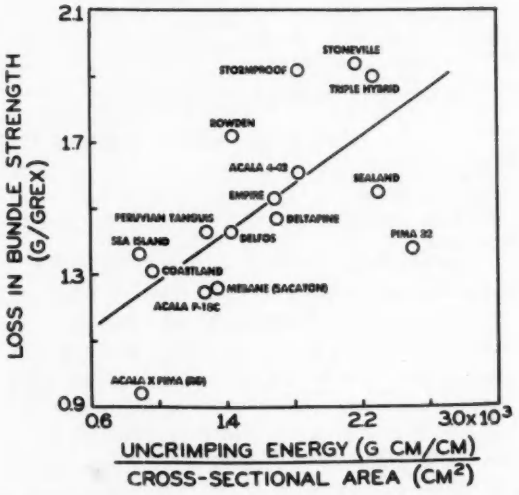

Fig. 8. Relation between fiber crimp and loss in Pressley bundle strength between zero and 5.0-mm. clamp spacing. Crimp per unit area measurements were made on unprocessed cotton.

Changes in fiber properties with processing of the cotton into yarn are of considerable interest in connection with the prediction of yarn behavior from measurements on the ginned stock. Small changes in the elongation to break occur, increasing in the early stages and later decreasing to values close to those found in the ginned cotton. These changes, however, are not large (about 7%) but follow a pattern found in a more extensive study of processing effects [6]. The steps in processing between sliver and yarn increase the elastic modulus of all cottons about 30%. This large increase in the modulus of fibers in yarn over the modulus of unprocessed cotton, and the lack of effect of processing on the strength and elongation values, suggest that it is the low load portion of the fiber stress-strain curve which is altered. Fiber crimp is appreciably modified by processing so that fibers in yarn have only about half the crimp which they originally had. Because of these processing effects it is not surprising that better correlation of fiber properties with the behavior of slivers and yarns are obtained when the fibers tested have been drawn from yarn rather than from unprocessed cotton. The improvement is not as great as might be expected, however, so that values obtained from unprocessed cotton can be used with nearly as good results.

The contribution of each fiber property to the behavior of assemblies is complicated by the fact that the fiber properties are interrelated. Two commonly measured fiber properties, the length and the fineness, can be related to all other fiber properties measured in this test, with long, fine fibers having less crimp, higher elastic moduli, and lower breaking loads than the coarser fibers. The strength of these correlations is not the same for all cottons. This may be due in part to actual differences between the varieties and in part to the limited number of fibers tested. In general, correlations between the properties within varieties and between means of different varieties have the same relations. Exceptions to this involve either the breaking load or the breaking stress. Within any one cotton the breaking load is related to the fineness, finer fibers being the weaker ones. Because of varietal differences, however, this is not true when the average breaking strengths of varieties are compared with their finenesses. "Weak" fibers of one cotton may be stronger than "strong" fibers of another cotton; hence there is no correlation of fineness and breaking load between varieties.

While simple correlations may be useful in studying relations between fiber properties, multiple correlations must be employed in studying the effects of the fibers on the yarns because of the interrelations mentioned above. In this way the contribution of individual properties can be separated out. In Equation 1 the breaking stress is of relatively low importance, as shown both by the partial correlation coefficient and the regression coefficient. The elimination of the stress as a variable leads to Equation 2, which is equally as good for predicting yarn strength. It is conceivable that something like this actually happens in the yarn. Under tension the fibers in a yarn are not all under the same load; factors such as the twist and the fiber position relative to the center of the yarn distribute the load so that some fibers carry more than others. These more highly loaded fibers reach their maximum strength sooner than others, at which time they break, and their share of the load is transferred to other, unbroken fibers. With a mechanism such as this it is possible that factors other than fiber strength may play a large role in determining the yarn strength. Yarn strength would then depend largely on the number of fibers and fiber ends at any given cross section, on the fiber-to-fiber friction (not evaluated here), and on the elastic (or extensional) properties of the fibers. Under such circumstances the very important part which elastic modulus appears to play in yarn strength is altogether reasonable.

In conclusion it should be emphasized that the results herein reported are for a limited number of cottons at one sliver and one yarn construction. Although the selection of cottons was fairly wide, it was limited to those grown in the United States and two comparison varieties. A broader study should include some of the very coarse Asiatic types of cotton.

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Appendix

Summary of Properties Measured

Test	Property	Definition	Units
Single fiber	Area of cross section	The average area of fiber cross section based on weight per unit length and a density of 1.53. The fiber is assumed to be round.	$cm.^2$
	Breaking load	Force required to break the fiber	g.
	Elongation to break	The extension of the fiber at the end of its force-extension curve divided by its original length	%
	Hookean slope	Slope of the initial straight line portion of the force-extension curve	g./%
	Crimp energy	Energy necessary to uncrimp the fiber	g. cm./cm.
	Energy to break	Energy required to rupture the fiber	g. cm./cm.
	Elastic modulus	Force necessary to elongate a fiber 1 $cm.^2$ in cross section 1%	$g./\%/cm.^2$
	Breaking stress	Force necessary to rupture the fiber per square centimeter of cross section	$g./cm.^2$
	Reversals	A change in the twist direction of the cellulose fibrils	rev./cm.
Pressley bundle	Strength	The force per unit weight necessary to break the bundle	g./grex
	Elongation	The extension of the bundle at break divided by its original length	%
Sliver	Maximum load	The peak load which the sliver will bear before pulling apart	g.
	Weight		grains/yd.
	Slope	Slope of the initial straight-line portion of the force-extension curve	g./%
Yarn	Breaking load	The force necessary to break the yarn	g.
	Breaking elongation	The extension of the yarn at break divided by its original length	%

Test Conditions

Single fiber, drawn from ginned cotton, finisher drawing sliver, and 36's carded yarns

Gauge length	½ in.
Crosshead speed	0.05 in./min.
Rate of extension	10%/min.
Chart speed	10 in./min.
Load range	2 g. full-scale (initial) 10 g. full-scale (final)

Area under the force-extension curve obtained by integrator on the Instron
Vibroscope data obtained during tensile test by attachment on the Instron

Pressley flat bundle tests on ginned cotton

Spacing between clamps	Crosshead speed
0.0 mm. (nominal)	0.02 in./min.
1.5 mm.	0.05 in./min.
5.0 mm.	0.10 in./min.

Instron machine fitted with holders for Pressley clamps

Finisher drawing sliver

Gauge length	10 in.
Crosshead speed	5 in./min.
Rate of elongation	50%/min.
Chart speed	10 in./min.
Load range	50 g. full-scale

Single end breaks on 36's carded yarns

Length between clamps	Crosshead speed
2 in.	1 in./min.
20 in.	10 in./min.

Instron machine fitted with Scott X-5 clamps

Evenness of sliver and yarn

Yarn or sliver speed	6 ft./min.
Chart speed	3 in./min.

Literature Cited

1. Am. Soc. Testing Materials, "Tentative Methods of Testing Cotton Fibers" (D414–52T), *A.S.T.M. Standards on Textile Materials,* Philadelphia, pp. 307–327 (1952).
2. Balls, W. L., *Studies of Quality in Cotton,* MacMillan, New York (1928).
3. Brown, H. M., TEXTILE RESEARCH JOURNAL **24**, 251 (1954).
4. Evans, T. F., and Montgomery, D. J., TEXTILE RESEARCH JOURNAL **23**, 689 (1953).
5. Gaus, G. E., and Larrison, J. E., *A Mechanical Cotton Fiber Blender for Use in Fiber Testing Laboratories,* mimeographed by Cotton Branch, P.M.A., U.S.D.A. (August 1951).
6. Grant, J. N., Morlier, O. W., and Scott, J. M., TEXTILE RESEARCH JOURNAL **22**, 682 (1952).
7. Gregory, J., *J. Textile Inst.* **44**, T499–514 (1953).
8. Gregory, J., *J. Textile Inst.* **44**, T515–33 (1953).
9. Hindman, H., and Burr, G. S., *Trans. Am. Soc. Mech. Engrs.* **71**, 789 (1949).
10. Montgomery, D. J., *J. Applied Phys.* **24**, 1092 (1953).
11. Montgomery, D. J., and Milloway, W. T., TEXTILE RESEARCH JOURNAL **22**, 729 (1952).
12. Platt, M. M., TEXTILE RESEARCH JOURNAL **24**, 132 (1954).
13. Platt, M. M., TEXTILE RESEARCH JOURNAL **20**, 519 (1950).
14. *Progress Report on the Annual Varietal and Environmental Study of Fiber and Spinning Properties of Cottons, 1951 Crop,* Bulletin of the Bureau of Plant Industry, Agricultural Research Administration, U.S.D.A. (July 1951).
15. Toner, R. K., *Textile Ind.* **116**, No. 9, p. 176 (1952).
16. Wakeham, H., and Spicer, N., TEXTILE RESEARCH JOURNAL **21**, 187 (1951); **25**, 585 (1955).
17. Wakeham, H., Virgin, W. P., and Spicer, N., TEXTILE RESEARCH JOURNAL **24**, 802 (1954).
18. Webb, R. W., and Richardson, H. B., "Relationships Between Properties of Cotton Fibers and Strength of Carded Yarns," U. S. Dept. Agr., War Food Admin., 58 pp. illus. (Processed, March 1945).
19. Webb, R. W., and Richardson, H. B., "Comparative Significance of Alternative Cotton Fiber Length and Strength Measure in Relation to Yarn Strength," U. S. Dept. Agr., Prod. and Mktg. Admin., 62 pp. illus. (Processed, September 1945).
20. Webb, R. W., Richardson, H. B., and Doretta, H., "Relation of Six Elements of Yarn Quality to Strength of 22's Yarn (Regular Draft) by Crop Year, Variety, and Staple Length," U. S. Dept. Agr., Prod. and Mktg. Admin., 61 pp. (Processed, October 1949).
21. Webb, R. W., and Richardson, H. B., "Relation of Six Elements of Raw Cotton Quality to Strength of 22's and 50's Yarn" (Long Draft), U. S. Dept. Agr., Prod. and Mktg. Admin., 63 pp. (Processed, April 1950).

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Cellulose Studies

Part XXI. The Rate of Degradation of Cellulosic Materials to the Oligosaccharide Stage in Phosphoric Acid Solution[1]

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Introduction

The hydrolytic degradation of cellulosic materials in various solutions has been the subject of a number of studies. Concentrated salt solutions [24] and mineral acids, such as superconcentrated hydrochloric acid [28], 51% sulfuric acid [7, 9], and 85% phosphoric acid [4, 5], have been employed as solvents for cellulose. These acids are reaction solvents which attack cellulose at the moment of first contact by the mechanism of hydrolytic degradation. In contrast to the other two acid solvents, phosphoric acid hydrolyzes cellulose at a comparatively slow rate. This slow reaction permits one to take many samples during the course of hydrolysis and thus follow the rate quite closely.

The rate of hydrolysis of cellulosic materials in phosphoric acid has been studied by several workers by measuring the change in the viscosity of the solutions with time.

The relation established by Staudinger between viscosity and molecular weight has been first applied to the homogeneous degradation of cellulose in phosphoric acid by af Ekenstam [4, 5]. The degree of polymerization, (D.P.), at any time t was calculated from the viscosity of the solution. The rate constant k for the hydrolysis could then be found by means of the relationship first derived by Freudenberg, Kuhn, and co-workers [6 through 9, 16],

$$k = 1/t \ln \frac{(1 - 1/\text{D.P.}_0)}{(1 - 1/\text{D.P.}_t)} \qquad (1)$$

where D.P._0 and D.P._t are the number-average degrees of polymerization of the cellulose at zero time and time t, respectively.

The assumptions made in deriving this equation are (a) that the starting material is composed of chains of a uniform finite length, (b) that the splitting of bonds is a first-order reaction, and (c) that all bonds are equally available for cleavage at the same rate.

Expansion of the right side of Equation (1) to an infinite series gives

$$kt = \left(\frac{\text{D.P.}_0 - \text{D.P.}_t}{\text{D.P.}_0 \cdot \text{D.P.}_t}\right) + \frac{1}{2}\left(\frac{\text{D.P.}_0^2 - \text{D.P.}_t^2}{\text{D.P.}_0^2 \cdot \text{D.P.}_t^2}\right) + \frac{1}{3}\left(\frac{\text{D.P.}_0^3 - \text{D.P.}_t^3}{\text{D.P.}_0^3 \cdot \text{D.P.}_t^3}\right) + \cdots.$$

In the *initial* stages of the hydrolysis all of the terms on the right side of the equation other than the first one may be neglected. One then obtains the equation in the form in which it has been used by many investigators [1, 2, 4, 5, 15, 27],

$$k = \frac{1}{t}\left(\frac{\text{D.P.}_0 - \text{D.P.}_t}{\text{D.P.}_0 \cdot \text{D.P.}_t}\right) = \frac{1}{t}\left(\frac{1}{\text{D.P.}_t} - \frac{1}{\text{D.P.}_0}\right) \qquad (2)$$

Af Ekenstam found that the rate of hydrolysis of cotton and sulfite pulp in phosphoric acid dropped rapidly from an initial high value to a considerably lower value which was relatively constant. Therefore, he concluded that there must be some "native" bonds present which are more rapidly hydrolyzed than the normal 1,4-β-glucosidic bonds. After these bonds, which he believed to be "esterlike," are broken in the cotton or the sulfite pulp, the rate of hydrolysis slows down to a constant value.

Stamm and Cohen [26] found a similar rapid initial rate of hydrolysis when they degraded cotton

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and wood pulp in phosphoric acid. In this work, the rate of hydrolysis was also followed viscometrically. The rate constant for the hydrolysis decreased after the first 6 hr. to a constant value of 7.05×10^{-6} min.$^{-1}$, which was claimed to be the rate of breaking of the normal 1,4-β-glucosidic bonds. No explanation was given by these authors for the observed rapid initial hydrolysis of the cotton and the wood pulp.

A sample of native cellulose, 80% of which was shown to consist of uniform chains with a D.P. of 3100 ± 100, was hydrolyzed in phosphoric acid by Schulz and Husemann [23]. These authors arrived at the conclusion that in cellulose molecules of a uniform chain length of 3100, there are five weak linkages which are rapidly split during acid hydrolysis to give rise to six fragments of a uniform chain length of D.P. $2^9 = 512$. It was postulated by Schulz and Husemann that these weak linkages were due to the presence in the cellulose chains of regularly spaced xylose anhydride units which were supposed to have formed from glucuronic acid units by decarboxylation. This decarboxylation reaction would presumably occur rapidly in the acid medium prior to the fast hydrolysis, since Schulz and Husemann refer to the carboxyl content of the starting material as evidence in support of their theory. Xylose anhydride units were proposed as the weak links because it was found that xylan, a polymer of xylose, is hydrolyzed at a rate 1500 times faster than cellulose [23]. However, special efforts made earlier by Irvine and Hirst [14] to detect pentoses in the acid hydrolysate of cellulose gave completely negative results.

Hiller and Pacsu [12], who likewise found a rapid initial drop in the viscosity of solutions of cotton in phosphoric acid, also attributed this behavior to the presence of some weak links in the structure of cellulose. These authors suggested that the weak links, corresponding to Haworth's unspecified "polymeric links" [11], might be acyclic acetal or hemiacetal bonds, which joined adjacent chains, probably by means of 1,5-linkages, to give rise to micellar laminae [19].

In a recent work on the heterogeneous and homogeneous hydrolysis of cellulosic materials, Jørgensen [15] concluded that cotton has no weak linkages, whereas more evidence is required to determine whether there are weak linkages in wood pulps. For the homogeneous hydrolysis in approximately 81% phosphoric acid at 25° C., the celluloses were first subjected to a 3- to 4-hr. preswelling period in 73.2% phosphoric acid at 0° C., after which 86.4% phosphoric acid was added to dissolve the samples. Complete solution was reached after 4 to 6 hr., but at that time the samples had already been in contact with the acid from 7 to 10 hr. The rates of hydrolysis of the three types of cellulose employed were determined by measuring the intrinsic viscosities of the solutions at certain intervals of time and converting the viscosity data to number-average D.P. values after the changes in relative nonuniformity during hydrolysis had been taken into consideration. However, the hydrolysis of cotton cellulose was studied over a period of 35 hr. only. Jørgensen reported that the D.P. of the starting material was 3930, but in the hydrolysis experiments he found a number-average D.P. of 1245 at zero time. At the end of the experiment, the D.P. was 54. Below D.P. 100 the rate increased; so these high values were omitted in calculating the average hydrolysis constant. Thus, the latter value, $k = 7.8 \times 10^{-6}$ min.$^{-1}$, represents a constant rate during 19 hr. only and through the relatively small drop of D.P. from 1245 to 104, with only 0.9% of the available bonds having been broken. Mitscherlich pulp similarly investigated gave a uniform hydrolysis constant of 15.8×10^{-6} min.$^{-1}$ for the first 5.5 hr., while the D.P. dropped from 550 to 142 (0.5% bonds broken). The aspen semichemical pulp gave a constant rate for an even shorter period of time. At the start the rate was fast, then after 15 min. it leveled off at 8.6×10^{-6} min.$^{-1}$ for 4 hr. over the narrow range of D.P. 597 to 269 (0.2% bonds broken). After that time the rate constant again increased. Jørgensen attributed the higher rate value for the Mitscherlich pulp to the presence of xylose anhydride units supposedly built into the glucose anhydride chains at irregular intervals. The large amount of carboxyl groups in the 6 positions of the glucose anhydride units in wood pulp, as found by Husemann and Weber [13], was not regarded as a possible cause for the faster rate of hydrolysis by Jørgensen who stated that "All evidences are that the introduction of such a carboxyl group greatly strengthens the interunit bond, because both pectinic and alginic acid are more resistant towards acid hydrolysis than are the corresponding anhydrosugar chains."

The constancy of the hydrolysis rates for the three celluloses was shown by plotting the change in the degree of splitting, ΔS, against time. Matthes [18] defines the degree of splitting as $S = 1/\text{D.P.}_n$. If

a small change in the degree of splitting is produced, one obtains

$$\Delta S = S_2 - S_1 = (1/\text{D.P.}_2 - 1/\text{D.P.}_1)$$

where D.P.$_1$ and D.P.$_2$ are the number-average D.P.'s of any two samples at the corresponding times t_1 and t_2, respectively. By introducing this expression in the nonlogarithmic equation

$$k' = 1/\Delta t(1/\text{D.P.}_2 - 1/\text{D.P.}_1) \qquad (3)$$

one obtains the relationship $k' = \Delta S/\Delta t$.

If ΔS is then plotted against Δt, a straight line should be obtained if k' is constant. Jørgensen's results show that straight lines are obtained only within an extremely narrow range of D.P. values and even then the initial values and the values toward the end of the measurements must be ignored.

A recent investigation carried on in this laboratory by Bauer and Pacsu [2] has cast doubt upon the validity of the rate constants found by previous workers for the hydrolysis of cellulose in phosphoric acid. These authors used the hydrolysis constants given by af Ekenstam [4, 5], Stamm and Cohen [26], Schulz and Husemann [23], and Jørgensen [15] to calculate the time required for the scission of 99% of the bonds in cellulose from the general equation, $kt = \ln(c_0/c_t)$, where c_0 and c_t are the per cent concentration of the hydrolyzable bonds at zero time and time t, respectively. At 99% completion of the reaction, $c_t = 0.01\ c_0$, therefore, $kt = \ln(1/0.01) = 4.605$. The time required to reach 99% completion, $t = 4.605/k$, was then calculated to be 400 to 500 days, depending upon the value of the chosen rate constant.

In contrast to the calculated time, however, Bauer and Pacsu found that after a solution of cellulose in 85% phosphoric acid had been allowed to react for 570 days at 21° C., 40% of the cellulosic material in the solution still precipitated out on dilution with water, and the fractions separated had D.P. values ranging from 72 to 307. From this experimental fact, the authors concluded that "there must be some error in the determination of the published rate constants for this hydrolysis, which predicts total conversion to glucose in less than 14 months, or else cellulose does not occur as a linear chain molecule in the phosphoric acid." They have suggested that the rates measured by previous workers between extremely narrow limits of D.P. values may be entirely due to the cleavage of freely accessible acid-sensitive bonds and, therefore, do not represent the presumably slower rate of hydrolysis of the 1,4-β-glucosidic bonds. Since the hydrolysis constant seems to increase as the size of the molecule decreases, as found by Freudenberg and co-workers [7, 9] and by other investigators [15, 23], one would expect that the total hydrolysis of cellulose to D-glucose should take place in a much shorter period of time than the one calculated from the available rate constants. As mentioned above, the opposite was found by experiments.

Statement of Problem

In order to gain more information as to the nature of this hydrolysis reaction, the present study was undertaken to determine the rate of decrease in the number-average degree of polymerization of viscose, regenerated cellulose and native hydrocellulose in 85% phosphoric acid during a major part of the hydrolytic process. An attempt was made to achieve a quantitative recovery of the degradation products from the hydrolysis of these cellulosic materials. By measuring the relative amounts of each of these products and determining the number-average D.P.'s from reducing end-group estimations, it was possible to obtain a combined average degree of ploymerization for each sample taken at suitable intervals of time. Thus, viscometry and osmometry were eliminated in the present work as means of following the course of the reaction.

The rate of hydrolysis of cellobiose in phosphoric acid was also determined to verify Freudenberg's findings that the 1,4-β-glucosidic bond of cellobiose is hydrolyzed three times faster than the same type bonds in the cellulose molecule.

Experimental Procedure

Preparation of Starting Materials

American Viscose Corporation's Avisco rayon bright viscose was used as one of the starting materials. The viscose was washed in 2% Dreft solution at 60° C. for 1 hr. to remove any impurities from the surface of the filament. It was then dried and ground to 10 mesh in the Wiley mill before solution in phosphoric acid. The D.P. of the viscose rayon was 384, determined by viscometry.

The regenerated hydrocellulose used in these experiments was obtained by hydrolyzing the above-mentioned viscose in 1 N hydrochloric acid at 60° C. for 24 hr. The resultant product was then rinsed thoroughly with water, washed twice with methanol,

and dried in the vacuum oven at 55° C. for 5 hr. By viscometric means, D.P. 52 was found.

The native hydrocellulose was obtained by similar hydrolysis of cotton which was received in the form of a sliver. The latter was first purified by the standard purification process used in this laboratory [27], then treated with 1 *N* hydrochloric acid for 24 hr. at 60° C. The native hydrocellulose produced by this method was washed twice with distilled water, thrice with methanol, once with ether, and then dried in the oven at 55° C. The D.P. of the native hydrocellulose was 288, determined by viscometry.

One per cent solutions, by weight, of each of the three cellulosic starting materials were prepared by dissolving 40 g. of each in 3960 g. of 85% phosphoric acid. In order to obtain optically clear solutions, it was necessary to stir the initial suspensions for several hours at room temperature. The solutions were then stored in dark bottles in a constant temperature room at 21° C.

Treatment of Samples Extracted from the Phosphoric Acid Solutions

One-hundred-gram samples were removed from each of the three phosphoric acid solutions at convenient intervals of time and were poured into separate beakers containing a mixture of 1000 g. of ice and water. Each mixture was stirred until all the ice had melted and was then refrigerated overnight.

It was found that all of the cellulosic materials having a number-average D.P. value greater than about 16 were precipitated by the dilution of the phosphoric acid solution. The precipitates were separated by repeated centrifugation in 50-ml. centrifuge tubes. The precipitates were then washed in the tubes several times with distilled water. Since it had been previously reported by Rånby [21] that with repeated washing of a sulfuric acid–treated cellulose the later washings became turbid owing to the peptization of "very small filterable cellulosic particles," care was taken to discontinue the operation as soon as any turbidity of the washings was noticed. The washings were added to the centrifugates. The precipitates were washed thrice with methanol, twice with ether, and then dried to constant weight in the vacuum oven at 55° C. These precipitates are designated as *primary* precipitates.

Neutralization of the centrifugates from the samples was then carried out by passing the clear solutions through a column packed with Amberlite ion exchange resin IR-4B (weak base). The column used was 3 cm. in diameter and was filled to a height of 70 cm. with the resin. Before each re-use, the resin was regenerated by passing 2 liters of 4% sodium hydroxide solution through the column. The latter was then washed with 4 liters of distilled water to remove any excess alkali, and backwashed with distilled water to ensure a uniform packing of the resin. The centrifugates, about 1200 ml. in volume, were passed through the ion exchange column to remove the phosphoric acid from the solutions. Following this, the column was washed with about 2 liters of distilled water. The washings were combined with the neutralized centrifugates.

In a preliminary experiment it was found that further precipitation of cellulosic material occurred upon evaporation of the neutralized centrifugates. For this reason, the latter were concentrated to a definite volume. A volume of about 100 ml. was arbitrarily chosen as the volume to which the solutions were condensed. The precipitates obtained by concentration of the neutralized centrifugates to a volume somewhat less than 100 ml. are designated as *secondary* precipitates.

The secondary precipitates were removed by centrifugation, washed thrice with methanol, twice with ether, and then dried to constant weight in the vacuum oven at 55° C. The methanol and ether washings were discarded.

The aqueous centrifugates from these secondary precipitates were brought to the mark in a 100-ml. volumetric flask. Aliquots of these solutions were then titrated with alkaline hypoiodite to determine the total reducing power of the water-soluble sugars present in each of the samples. The measurements were carried out essentially under the conditions recommended by Blom and Rosted [3] with the exception that the reaction time was extended to 60 min.

For determination of the total glucose after hydrolysis of the oligosaccharides present in the above solutions, aliquots of the latter were treated with hydrochloric acid (final acidity 1 *N*) for 6 hr. at 100° C. to hydrolyze all of the oligosaccharides to D-glucose. The hydrolyzed samples were neutralized with dilute alkali, and then the total weight of glucose in the samples was determined by the hypoiodite procedure mentioned above. From the values so obtained, it was possible to calculate the per cent of the weight of the original cellulosic material which had been hydrolyzed in the phosphoric acid solution to water-soluble saccharides at the given time. Fur-

thermore, the ratio of the reducing power of the centrifugates after complete hydrolysis to the reducing power of the centrifugates before hydrolysis gave the number-average D.P.'s of the saccharides present in the centrifugates.

Thus, each sample is divided into three parts: the primary precipitate, the secondary precipitate, and the water-soluble saccharides. The percentages of the original cellulosic material which are present as primary and secondary precipitates at a given time may be obtained directly from the weights of these precipitates. The amount of the original cellulosic material which has been hydrolyzed to the stage of soluble saccharides at a given time may be obtained from the total millimole glucose present in the centrifugate after complete hydrolysis by multiplying millimoles by 162, the equivalent weight of a glucose anhydride unit.

In the large number of measurements involving quantitative isolation and drying to constant weight of frequently very small samples, some values were clearly invalidated by experimental errors in the handling of the material. Data obtained from such experiments were excluded from the calculation of the rate constants.

The number-average D.P.'s of the primary and secondary precipitates were measured by reducing end-group estimation. Alkaline hypoiodite was used as the titrating agent, and the procedure was that described by Martin, *et al.* [17] for the end-group estimation of hydrocellulose. In the titrations of the precipitates, an excess of 300% of the iodine reagent was employed.

Calculation of the Combined Average Degree of Polymerization

The values of the number-average D.P.'s for the primary precipitates, when plotted against time, gave a smooth curve that fitted to all the points. From this curve the number-average D.P. values of the primary precipitates were obtained by reading off the values for the desired time t. By similar treatment of the number-average D.P. values obtained from the secondary precipitates of the regenerated hydrocellulose and native hydrocellulose samples, the D.P. values for any time t were read from the respective curves. In calculating the combined average D.P.'s of the viscose samples, only the experimentally determined D.P. values of the secondary precipitates were used, since no adequate curve could be fitted to the experimental points. In general the number-average D.P.'s of the secondary precipitates showed a tendency to level off at about D.P. 8.

The ratio of the reducing value of total glucose present after complete hydrolysis of the sugars in the neutral centrifugate to the reducing value of the sugars before hydrolysis represents the number-average D.P. of the various saccharides present in the neutral centrifugate.

From the weights of the primary and secondary precipitates and of the starting materials calculated from the total glucose values of the centrifugates, and from the corresponding D.P. values as found above, it was possible to calculate the combined number-average degree of polymerization of each sample by means of the equation

$$\text{D.P.} = \frac{(\text{D.P.}_\text{I})(\text{P}_\text{I}) + (\text{D.P.}_\text{II})(\text{P}_\text{II}) + (\text{D.P.}_s)(\text{P}_s)}{P_t} \quad (4)$$

where D.P._I, D.P._II, and D.P._s are the number-average degrees of polymerization of the primary precipitate, secondary precipitate, and of the saccharides in the centrifugate, respectively; and, P_I, P_II, and P_s are the percentages of the original starting material from which each of these portions has derived. P_t is the total per cent of the original material recovered.

All the experimental data obtained in this work are summarized in Tables I through III for viscose, regenerated hydrocellulose, and native hydrocellulose, respectively.

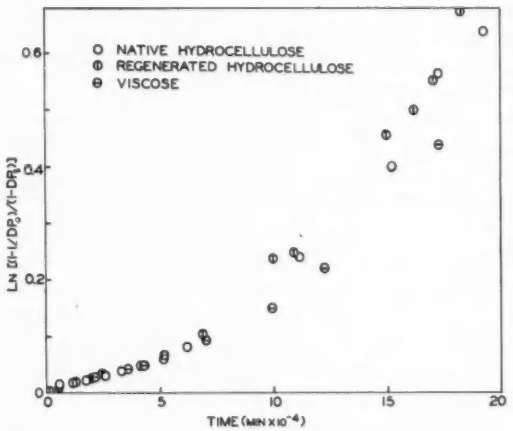

Fig. 1. Homogeneous acid degradation of cellulosic materials in 85% phosphoric acid at 21° C.

Rate of Decrease of the Combined Number-Average D.P.'s of the Cellulosic Material

The rate of hydrolysis of the cellulosic material may be calculated from Equation 1, where $D.P._{\cdot 0}$ and $D.P._{\cdot t}$ represent the combined number-average degrees of polymerization obtained by means of Equation 4. These D.P. values, together with the values of $\ln[(1 - 1/D.P._{\cdot 0})/(1 - 1/D.P._{\cdot t})]$ and the values of k are shown in Tables IV through VI. The values of the logarithmic function for viscose, regenerated hydrocellulose, and native hydrocellulose are plotted against time in Figure 1.

The rate constants k' for the hydrolysis have also been determined between the limits of two consecutive times, t_2 and t_1, from the corresponding combined average degrees of polymerization, $D.P._{\cdot 2}$ and $D.P._{\cdot 1}$, by means of equation

$$k'(t_2 - t_1) = \ln \frac{(1 - 1/D.P._{\cdot 1})}{(1 - 1/D.P._{\cdot 2})}$$

The values of the logarithmic function and of the corresponding rate constants k' are given in the last two columns of Tables IV through VI.

Hydrolysis of Cellobiose in Phosphoric Acid

A 1% solution of cellobiose in 85% phosphoric acid was prepared by dissolving 5 g. of cellobiose in 495 g. of the acid. The solution was kept in a constant temperature room at 21° C. Samples of 80 g. each were extracted from this solution at convenient intervals of time and poured into 500 ml. of a mixture of ice and water. The samples were then neutralized by passing them through a column packed

TABLE I. Percentages and D.P. Values of Products Recovered from 85% Phosphoric Acid Solution of Viscose as Primary and Secondary Precipitates and as Water-Soluble Simple Sugars

Time (days)	Ppt. I (%)	D.P. of ppt. I by titration	Ppt. II (%)	D.P. of ppt. II by titration	Water-sol. sugars (%)	D.P. of sugars	Total recovery (%)
4	94.1	—	0.7	—	—	—	—
5	—	56	—	—	3.5	2.0	—
6	91.8	—	1.7	—	4.4	2.5	97.9
7	—	—	—	—	4.6	2.6	—
8	89.1	—	2.1	—	5.5	2.6	96.7
9	—	48	—	—	6.3	2.2	—
11	87.1	—	(1.2)	—	6.4	—	(94.7)
13	—	—	4.2	—	8.0	2.4	—
15	81.4	—	4.6	10	(13.4)	1.9	(99.4)
18	—	34	7.3	—	10.8	3.0	—
20	75.2	—	—	—	—	—	—
22	73.1	—	8.8	—	13.4	2.7	95.3
25	66.4	—	(15.5)	18	13.4	—	(95.3)
27	64.4	26	11.1	—	17.6	3.0	93.1
30	59.5	—	(13.7)	14	20.0	2.8	(93.7)
33	54.7	—	14.1	—	—	—	—
36	51.0	—	(17.0)	12	25.2	2.6	(93.2)
40	—	22	—	—	26.8	2.7	—
44	40.3	—	20.6	—	28.5	2.6	89.4
49	(37.1)	—	21.0	8	31.0	2.5	(89.1)
54	26.8	19	—	—	37.9	2.5	—
60	18.3	—	—	—	—	—	—
62	15.9	—	30.9	—	40.5	2.4	87.3
69	8.7	20	(27.2)	12	44.9	2.5	(80.8)
78	(8.0)	—	—	—	52.2	2.3	—
85			26.6	11	57.3	2.4	83.9
92			22.3	—	57.5	2.0	79.8
101			17.3	13	—	—	—
120			12.0	8	72.2	2.0	84.2
129			—	—	72.0	1.9	—
141			4.2	—	—	—	—
155			3.0	—	78.9	1.7	81.9
170			1.5	—	79.5	1.6	81.0

TABLE II. Percentages and D.P. Values of Products Recovered from 85% Phosphoric Acid Solution of Regenerated Hydrocellulose as Primary and Secondary Precipitates and as Water-Soluble Simple Sugars

Time (days)	Ppt. I (%)	D.P. of ppt. I by titration	Ppt. II (%)	D.P. of ppt. II by titration	Water-sol. sugars (%)	D.P. of sugars	Total recovery (%)
1	90.5	39	4.5	—	4.3	2.7	99.3
2	—	—	—	—	5.6	2.0	—
4	87.0	38	5.2	—	6.5	3.1	98.7
6	85.2	—	(7.8)	14	8.7	2.5	(101.7)
8	80.4	—	7.7	—	9.2	2.9	97.3
11	76.6	31	9.2	—	(7.6)	—	(93.4)
14	70.9	27	10.5	15	13.4	2.6	94.8
17	65.2	—	14.0	—	18.2	3.1	97.4
20	—	—	—	—	21.4	2.7	—
27	49.2	23	18.6	10	—	—	—
34	42.6	—	17.5	—	—	—	—
41	33.7	—	18.1	—	—	—	—
48	23.8	18	22.1	—	37.0	2.3	82.9
55	11.0	—	(20.2)	9	42.8	2.5	(74.0)
62			31.0	—	(56.1)	2.4	(87.1)
70			27.5	—	52.3	2.2	79.8
76			21.3	—	62.1	2.2	83.4
83			18.6	8	—	—	—
98			12.3	8	—	—	—
104			9.8	—	68.9	1.9	78.7
113			7.5	—	74.6	2.0	82.1
119			6.1	7	77.9	2.0	84.0
127			3.7	—	80.3	1.8	84.0
134			(3.7)	—	(72.9)	1.6	(76.6)
141			1.8	—	82.7	1.8	84.5

TABLE III. Percentages and D.P. Values of Products Recovered from 85% Phosphoric Acid Solution of Native Hydrocellulose as Primary and Secondary Precipitates and as Water-Soluble Simple Sugars

Time (days)	Ppt. I (%)	D.P. of ppt. I by titration	Ppt. II (%)	D.P. of ppt. II by titration	Water-sol. sugars (%)	D.P. of sugars	Total recovery (%)
1	(98.9)	56	—	—	—	—	—
2	94.0	—	(1.2)	—	1.6	—	(96.8)
4	93.0	60	1.6	—	2.6	2.1	97.2
6	—	—	—	—	3.7	2.0	—
9	89.0	—	2.0	—	4.9	2.0	95.9
12	83.7	41	2.5	—	6.5	2.2	92.7
15	79.5	—	(4.8)	11.3	8.5	2.3	(92.8)
18	77.1	—	4.6	—	11.5	2.4	93.2
23	70.5	30	5.2	—	14.8	2.4	90.5
30	61.0	—	7.9	—	19.9	2.7	88.8
36	54.2	—	9.7	8.5	25.6	2.5	89.5
43	42.5	19	15.0	—	30.3	2.4	87.8
57	26.5	—	18.4	7.8	—	—	—
64	16.9	17	20.1	—	—	—	—
71	11.0	—	(23.1)	—	36.1	2.0	(70.2)
78	5.8	—	20.1	8.1	50.3	2.0	76.2
85	(5.8)	—	(17.4)	—	55.1	2.0	(78.3)
93			18.1	—	—	—	—
99			15.8	7.7	—	—	—
106			13.6	—	66.7	2.0	80.3
114			9.9	8.2	—	—	—
120			7.9	—	68.6	1.7	76.5
127			(7.2)	7.8	70.2	1.7	(77.4)
134			4.5	—	76.1	1.8	80.6

with Amberlite IR-4B, ion exchange resin. After neutralization the samples were concentrated under reduced pressure to a volume of 50 ml. The D-glucose and the cellobiose in the samples were chromatographically separated on paper, and each sugar was then titrated with alkaline hypoiodite according to the procedure described by Rebenfeld and Pacsu [22]. From the amounts of iodine consumed by either or both of these sugars, the per cent of cellobiose which had been hydrolyzed to glucose was

TABLE IV. Rate of Hydrolysis of Viscose from the Combined D.P.'s of Products in 85% Phosphoric Acid Solution

Time (days)	Combined av. D.P.	$\ln \frac{(1-1/D.P._0)}{(1-1/D.P._t)}$	$k \cdot 10^6$ (min.$^{-1}$)	$\ln \frac{(1-1/D.P._1)}{(1-1/D.P._2)}$	$k' \cdot 10^6$ (min.$^{-1}$)
0	384	—	—	—	—
15	32	0.0291	1.3	0.0291	1.35
25	23	0.0418	1.1	0.0127	0.88
30	19	0.0515	1.2	0.0097	1.34
36	15	0.0664	1.2	0.0149	1.72
49	11	0.0927	1.3	0.0263	1.40
69	7	0.1515	1.5	0.0588	2.04
85	5	0.2205	1.8	0.0690	3.00
120	2.8	0.4393	2.5	0.2188	4.34

TABLE V. Rate of Hydrolysis of Regenerated Hydrocellulose from the Combined D.P.'s of Products in 85% Phosphoric Acid Solution

Time (days)	Combined av. D.P.	$\ln \frac{(1-1/D.P._0)}{(1-1/D.P._t)}$	$k \cdot 10^6$ (min.$^{-1}$)	$\ln \frac{(1-1/D.P._1)}{(1-1/D.P._2)}$	$k' \cdot 10^6$ (min.$^{-1}$)
0	52.0	—	—	—	—
1	39.5	0.0062	4.3	0.0062	4.3
4	32.5	0.0118	2.0	0.0056	1.3
8	27.7	0.0173	1.5	0.0055	0.9
14	22.7	0.0255	1.2	0.0082	1.0
17	20.0	0.0323	1.3	0.0068	1.6
48	8.54	0.1051	1.5	0.0727	1.6
70	4.40	0.2384	2.3	0.1333	4.2
76	3.82	0.2505	2.3	0.0120	1.4
104	2.64	0.4567	3.0	0.2062	5.1
113	2.46	0.5023	3.1	0.0456	3.5
119	2.30	0.5512	3.2	0.0488	5.6
127	2.00	0.6738	3.6	0.1226	10.6

TABLE VI. Rate of Hydrolysis of Native Hydrocellulose from the Combined D.P.'s of Products in 85% Phosphoric Acid Solution

Time (days)	Combined av. D.P.	$\ln \frac{(1-1/D.P._0)}{(1-1/D.P._t)}$	$k \cdot 10^6$ (min.$^{-1}$)	$\ln \frac{(1-1/D.P._1)}{(1-1/D.P._2)}$	$k' \cdot 10^6$ (min.$^{-1}$)
0	288.0	—	—	—	—
4	57.2	0.0142	2.4	0.0142	2.4
9	43.3	0.0200	1.5	0.0058	0.8
12	38.2	0.0230	1.3	0.0031	0.7
18	29.5	0.0310	1.2	0.0080	0.9
23	24.5	0.0382	1.1	0.0072	1.0
30	19.0	0.0506	1.1	0.0124	1.2
36	15.5	0.06321	1.2	0.0125	1.4
43	12.2	0.0821	1.3	0.0189	1.8
78	4.6	0.2423	2.1	0.1602	3.2
106	3.0	0.4071	2.6	0.1648	4.0
120	2.3	0.5638	3.3	0.1567	7.8
134	2.1	0.6432	3.3	0.0794	3.9

obtained. The rate of hydrolysis was calculated from

$$kt = \ln[(100)/(100 - x)] \qquad (5)$$

The values of time, per cent (x) completion of the reaction, $\ln[(100)/(100 - x)]$ and the rate of hydrolysis, k, are given in Table VII. When $\ln[(100)/(100 - x)]$ was plotted against time, the mean value of the rate constant, $k = 11.1 \times 10^{-6}$ min.$^{-1}$, was obtained from the slope of the resulting straight line.

Discussion of Results

Most previous studies of the hydrolysis of cellulosic materials in phosphoric acid were discontinued after a D.P. of about 100 was reached, at which time less than 1% of the available bonds had been broken. In some instances, as in the case of the aspen semichemical pulp [15], the number of bonds broken during the reaction did not amount to more than 0.2% of the total number of hydrolyzable bonds present. Likewise, the time of observation was seldom extended beyond 24 hr.; for the most part, it was restricted to less than one day, occasionally only to a few hours. Even then the calculated mean constants for such inordinately short periods of the hydrolytic reaction appeared to be constant only by omission of the deviating initial and final values. Either the faster initial rates were considered to be of great importance, and attributed to the existence of some "weak" linkages in cellulose, or professed to be "not real," or ignored. The increase in the hydrolysis constants has usually been explained on the basis of Freudenberg's results, according to which the glycosidic bonds located near the ends of the chains suffer cleavage three times faster than those in the center. Although Freudenberg obtained this result on a material with an initial D.P. of about 50, his finding was frequently invoked for materials with D.P.'s of several hundreds [15].

TABLE VII. Hydrolysis of Cellobiose in 85% Phosphoric Acid Solution at 21° C.

Time (min.)	% Completion of reaction (x)	$\ln[(100)/(100-x)]$	$k \cdot 10^{-6}$ min.$^{-1}$
0	0	—	—
3410	4.3	0.0439	12.9
7665	6.9	0.0716	9.3
13385	15.6	0.1697	12.7
18040	17.7	0.1948	10.8

If the rate constant found for these short periods of time at the start of the reaction were valid for the remaining 99% or more of the total hydrolytic process, then by simple calculation from general Equation 5, one should find the time when the degradation products consisted of low-molecular-weight oligosaccharides and D-glucose only. It has been mentioned earlier that Bauer and Pacsu obtained in 40% yield insoluble fractions possessing D.P.'s between 307 and 72 from a 19-month old phosphoric acid solution of cotton cellulose, although the solution should have contained nothing but pure glucose after 14 months, if the rate of the reaction remained constant during the entire process, and considerably less than 14 months if the Freudenberg effect was taken into consideration.

For these reasons it was decided to study a major portion of the hydrolytic process as far as it was experimentally practicable. However, it appeared to us that measurements of the changes in viscosity did not constitute a suitable method to follow the course of the reaction. Particularly, when the degradation reaches the stage of production of a number of low D.P. material, the latter exerts only a negligible effect on the fluidity of the system. Consequently, the number of bonds actually broken cannot be directly correlated with the viscosity of such solutions. Moreover, the necessary determination of the relative nonuniformity of the samples, a property expressing the ratio between the viscosity-average and number-average D.P.'s, is a cumbersome procedure introducing new sources of experimental error. Estimation of the number-average D.P.'s of the nitrated samples would likewise give unsatisfactory and misleading results because the rapid diffusion of the small molecules through the membrane would cause grave errors in the osmotic pressure measurements.

In view of these difficulties, it was decided that the progress of the reaction would best be followed by direct determination of the weights and, by end-group analysis, of the number-average D.P.'s of both the water-insoluble and water-soluble materials present in the samples. From the data so obtained, a combined number-average D.P. of the products making up the system can be calculated. In producing the precipitates from the samples by dilution with water, the unexpected observation was made that degradation products with D.P.'s below 16 existed in peptized state in the de-ionized solutions. When flocculation by evaporation of such solutions was

accomplished, the material, designated as secondary precipitate, remained insoluble in water. It was also noted with interest that the D.P. of these secondary precipitates fell from 16 to about 7 or 8 in about 30 to 40 days to remain at that level for the rest of the reaction.

Inspection of the k and k' values shown in Tables IV to VI and the shape of the curves in Figure 1 leaves no element of doubt about the fact that the rate "constants" for the hydrolysis of viscose, regenerated hydrocellulose, and native hydrocellulose are not constant throughout the hydrolysis. It is seen from the data that the minimum value of the rate constant, $k = 1.1 \times 10^{-6}$ min.$^{-1}$, is one-seventh of the value $k = 7.8 \times 10^{-6}$ min.$^{-1}$ found by previous investigators for the hydrolytic degradation process. It is also evident that the latter value, valid for the first short phase of the reaction, decreases to the minimum value in about two to three weeks after the start of the reaction. After a total reaction time of about 40 days, the constant increases eventually to reach, as in the case of regenerated hydrocellulose, the rate constant $k = 11.1 \times 10^{-6}$ min.$^{-1}$ for the hydrolysis of cellobiose.

The gradual change in the hydrolysis constant during the whole process is clearly illustrated in Figure 2, where the k' values for the intervals between two consecutive times were plotted against log t, the latter having been used to put all the data in one graph. For regenerated hydrocellulose the minimum value of k' was 0.9×10^{-6} min.$^{-1}$ at D.P. 28, for viscose 0.8×10^{-6} min.$^{-1}$ at D.P. 23, and for hydrocellulose 0.7×10^{-6} min.$^{-1}$ at D.P. 38. It may be concluded, therefore, that the cellulosic materials under study, irrespective of their initial D.P.'s, behave in a like manner.

The minimum values for k' are smaller by a factor of 12 to 16 than the rate constant, $k = 11.1 \times 10^{-6}$ min.$^{-1}$, found for cellobiose. On the basis of the "end-group effect," it is possible to account for a threefold rise only in the value of k'. No explanation can be offered for the observed drop to one-eleventh, $k' = 0.7 \times 10^{-6}$ min.$^{-1}$, of the reported initial value, $k = 7.8 \times 10^{-6}$ min.$^{-1}$. On the basis of free accessibility and uniformity of the glycosidic bonds in the single-chain molecules, assumed to be present in a cellulose solution, such a behavior cannot be readily understood.

In searching for an acceptable interpretation of these results, one may consider various possibilities that could account for the peculiar behavior of cellulose in phosphoric acid solution. At this point, it should be noted that the materials used in the present study were already degraded to a considerable extent. It is therefore probable that native cellulose with its high degree of polymerization would have shown still greater deviation from the expected constancy of the k values.

If one wishes to adhere to the theory that cellulose consists of freely accessible single-chain molecules in solution, then one has to examine the possible causes of the difference in the scission rate of the glycosidic bonds in the light of this theory. The first point to be examined is the possible presence of foreign sugars built in a random or regular manner into the cellulose chain, as it was suggested by Schulz and Husemann and by other investigators. This possibility is to be ruled out, since no foreign sugar, notably xylose, has ever been reported to be present in pure cellulose, although special efforts have been made for its detection [14]. In this laboratory a large number of paper-chromatographic analyses performed on hydrolysates of cellulose or derivatives gave completely negative results for xylose or any other simple sugar except D-glucose.

Another suggestion by Schulz and Husemann, namely, the presence of glucuronic acid units in the chain, does not seem to be helpful either, since it

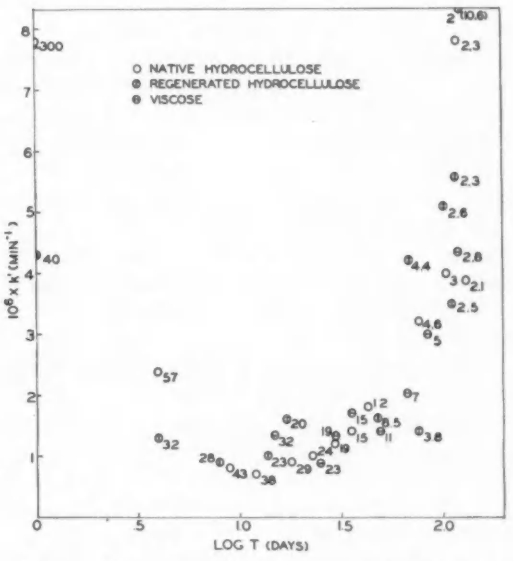

Fig. 2. Change in the hydrolysis constant during homogeneous acid degradation of cellulosic materials in 85% phosphoric acid at 21° C.

is well known that such units show a remarkable resistance toward hydrolytic scission.

The occurrence of random or regularly spaced glucofuranose units in the chain is another possibility that might be considered. Furanosides, in general, are hydrolyzed from 50 to 200 times more easily than the corresponding pyranosides [10], although exceptions are known [20], where the difference in the rates is not more than tenfold. If the cellulose chain indeed contained some glucofuranose anhydride units, then methylation and subsequent hydrolysis would still yield 2,3,6-trimethylglucose only, provided that the respective glucosidic linkages are of the 1,5 type. In such a case the presence of furanoid units would remain undetected by the methylation technique. To be sure, connection by some other type of linkage, such as a 1,6-β-bond between furanoid and pyranoid units, would result in the formation of 2,3,4-trimethylglucose and also in the presence of gentiobiose, a less readily hydrolyzable type of disaccharide unit built in the chain. Although these possibilities cannot be ruled out from consideration, at present they lack factual support and remain highly speculative. In any case, the presence in the chains of "weak" links, which presumably the furanoid units would represent, might be used to explain the initial fast rate of the reaction, but this could not be used for explanation for the large increase in the rate of the reaction when most or all of these weak bonds have been cleaved.

There is a further point that deserves consideration. It has been suggested often that in certain concentrations, cellulose solutions contain badly entangled chain molecules which would make some units inaccessible to a reagent. It seems to us highly improbable that such a situation would prevail in a 1% solution of regenerated hydrocellulose viscose or native hydrocellulose with their comparatively low degree of polymerization. Even in the case of native cellulose with D.P. values of several thousand, it is hardly conceivable that the solvent molecules would not have complete access to the individual chains, however entangled the latter may be.

If, on the other hand, one is ready to accept the view that cellulose is not dispersed molecularly in solution, then it would logically follow that all of the units are not available for reaction. Thus, by abandoning the basic postulate of molecular dispersion, one may consider the problem in the light of the micellar theory of cellulose structure. If the cellulose solution were micellar, where a micelle is first considered to be an aggregate of chain molecules, then the inner core of the crystalline portion would be less accessible than the surface and the so-called amorphous region of the micelle. In such a case, one would expect that the hydrolytic scission would preferentially occur in the accessible regions and on the surface of the crystallites resulting in higher rate constants. The comparatively slow penetration or diffusion of the phosphoric acid into the inner core of the micelle would cause delayed reaction, hence a slower rate. Increasing penetration of the phosphoric acid molecules into the swollen micell would manifest itself in an increasing rate constant which, after complete disintegration of the residual micelle, should not only reach the original value but also surpass it by approaching the value of k for cellobiose. Essentially, the whole process would resemble the heterogeneous acid degradation of cellulosic materials, although the degree of heterogeneity would be of different order of magnitude, and no limiting values would be possible.

The application of the theory of topochemical reaction to the cellulose micelle in solution, however, would raise the question concerning the nature of the forces operating between the individual chains in such a manner as to prevent their disintegration in strong acids, such as phosphoric acid. It is not likely that these intermolecular forces are hydrogen bonds, since these would not be expected to survive in the acid solution. However, the intermolecular forces may be covalent bonds which would make, in fact, the entire micelle a giant molecule. These bonds may be the open-chain acetal type as suggested by Pacsu or any other true covalent bonds such as Haworth's "polymeric bond" [11] which cross-link the cellulose chains into a three-dimensional micelle. In such a case the cellulose micelle would represent the fundamental molecule, and the distinction between a molecular and a micellar solution would disappear.

From this concept it would follow that *all* the reactions of cellulose in solvents take place on particles and not on simple, long chains of glucose anhydride units. Evidently, independent investigations are necessary in order to ascertain the molecular state of cellulose in acidic solutions. High-speed centrifugation, flow birefringence, electron microscopy, and light scattering have been recommended by Spurlin [25] to study this problem further.

Summary

1. Most previous studies of the hydrolysis of cellulosic materials have been carried out on samples with D.P. more than 1000 by using viscometry as a means of following the course of the reaction. The measurements were discontinued after a D.P. of about 100 was reached, when less than 1% of the available bonds had been broken. The time of observation has seldom extended beyond 24 hr.; in most cases it has been restricted to less than one day, occasionally to only a few hours. Even for such a short period of hydrolysis, the calculated rate constants appeared to be constant only by omission of the deviating initial and final values.

2. In the present work a major part, about 50%, of the reaction has been studied on comparatively low-molecular-weight materials such as viscose (D.P. 384), regenerated hydrocellulose (D.P. 52) and native hydrocellulose (D.P. 288), under identical conditions. The reaction was followed by precipitation of the products on ice at suitable intervals of time. All cellulosic materials with D.P. greater than about 14 to 16 precipitated out of the solution. After removal by centrifugation of these "primary" precipitates, deionization and concentration of the aqueous solutions gave rise to "secondary" precipitates of D.P. 7 to 16. In the remaining solutions the weights of the reducing sugars were determined by iodine titration. From the weights of the components and their number-average D.P.'s determined by reducing end-group analysis, the combined number-average D.P. values of the individual samples at t time were obtained.

3. From these D.P. values the rates of decrease of the combined number-average D.P.'s for the entire length of the process were calculated. When plotted against time, the initially high values of the rate constant rapidly decrease to a minimum reached after the first two or three weeks of the reaction, then gradually increase, finally approaching the value of k for cellobiose. All three cellulosic samples gave essentially identical results. The minimum value of $k' = 0.7 \times 10^{-6}$ min.$^{-1}$ found for hydrocellulose is about 11 times smaller than the reported value of $k = 7.8 \times 10^{-6}$ min.$^{-1}$ for cotton cellulose, and about 16 times smaller than the rate constant, $k = 11.1 \times 10^{-6}$ min.$^{-1}$, found for cellobiose.

4. For explanation of this peculiar behavior, several possibilities may be considered. On the basis of the theory of molecular dispersion of single-chain molecules in the acid solution, the initial drop in the values could not be interpreted without making the experimentally unsupported claim that easily hydrolyzable foreign elements, such as xylose anhydride units or glucuronic acid units, are incorporated in the chains. Likewise, assumption of glucofuranose anhydride units or 1,6-type bonds in the chain would not be helpful, since even if it were possible to find experimental evidence for such units, it would not explain the sixteenfold rise in the k values in the later part of the reaction.

5. An extension of the theory of micellar structure in the solid state to the solutions of cellulose and assumption of certain type of covalent bonds in the chains for holding the latter together in a three-dimensional micelle would offer a simple explanation for the nonconstancy of the k values. If the micelle were indeed one giant molecule of cellulose, then all the topochemical reactions observed in the heterogeneous reactions would take place with the same mechanism in the "homogeneous" reactions with the exception that the degree of heterogeneity in the latter case would be by orders of magnitude less than in the visibly heterogeneous systems.

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Literature Cited

1. Battista O. A., *Ind. Eng. Chem.* **42**, 502 (1950).
2. Bauer, F. W., and Pacsu, E., TEXTILE RESEARCH JOURNAL **22**, 397 (1952).
3. Blom, J., and Rosted, C. O., *Acta Chem. Scand.* **1**, 32 (1947).
4. af Ekenstam, A., *Ber.* **69B**, 549 (1936).
5. af Ekenstam, A., *Ber.* **69B**, 553 (1936).
6. Freudenberg, K., *Trans. Faraday Soc.* **32**, 74 (1936).
7. Freudenberg, K., and Blomqvist, G., *Ber.* **68B**, 2070 (1935).
8. Freudenberg, K., and Kuhn, W., *Ber.* **65B**, 484 (1932).
9. Freudenberg, K., Kuhn, W., Durr, W., Bolz, F., and Steinbrunn, G., *Ber.* **63B**, 1510 (1930).

10. Haworth, W. N., *Ber.* **65A**, 50 (1932).
11. Haworth, W. N., *J. Soc. Chem. Ind.* **58**, 917 (1939).
12. Hiller, L. A., Jr., and Pacsu, E., TEXTILE RESEARCH JOURNAL **16**, 564 (1946).
13. Husemann, E., and Weber, O. H., *J. prakt. Chem.* **159**, 334 (1942).
14. Irvine, J. C., and Hirst, E. L., *J. Chem. Soc.* **121**, 1585 (1922).
15. Jørgensen, L., "Studies on the Partial Hydrolysis of Cellulose," Oslo, Trykt Hos Emil Moestue A/S (1950).
16. Kuhn, W., *Z. physik. Chem.* **159**, 368 (1932).
17. Martin, A. R., Smith, L., Whistler, R. L., and Harris, M., *J. Research Natl. Bur. Standards* **27**, 449 (1941).
18. Matthes, A., *Kolloid-Z.* **98**, 319 (1942).
19. Pacsu, Eugene, in "Progress in the Chemistry of Organic Natural Products," Vol. V (L. Zechmeister, editor), Vienna, Springer-Verlag, p. 128 (1948).
20. Purves, C. B., and Hudson, C. S., *J. Am. Chem. Soc.* **59**, 1170 (1937).
21. Rånby, B. G., *Discussions Faraday Soc.* **11**, 158 (1951); *Acta Chem. Scand.* **3**, 649 (1949).
22. Rebenfeld, L., and Pacsu, E., TEXTILE RESEARCH JOURNAL **24**, 941 (1954).
23. Schulz, G. V., and Husemann, E., *Z. physik. Chem.* **52B**, 23 (1942).
24. Sihtola, H., "Eine Untersuchung über die Hydrolyse der Cellulose in Konzentrierten $ZnCl_2$—Lösungen," Helsinki (1944).
25. Spurlin, H. M., TEXTILE RESEARCH JOURNAL **22**, 693 (1952).
26. Stamm, A. J., and Cohen, W. E., *J. Phys. Chem.* **42**, 921 (1938).
27. Steele, R., and Pacsu, E., TEXTILE RESEARCH JOURNAL **19**, 771 (1949).
28. Willstätter, R., and Zechmeister, L., *Ber.* **46**, 2403 (1913).

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Dimensional Changes and Related Phenomena in Wool Fibers under Stress[1]

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Abstract

The type and magnitude of dimensional changes occurring in wool fibers under stress were investigated by means of transverse and longitudinal measurements. The over-all rate of decrease in the fiber diameter as related to the rate of extension indicated a constant volume distortion beyond the Hookean extension. However, slight deviations at approximately 5 and 27% extensions suggested the possibility of drastic structural changes at these levels. Data on the length contraction owing to crimp and observations at microscopic level regarding the absence of mechanical damages to the structural elements of wool under stress also are presented.

Introduction

Wool exhibits both crystalline and viscous characteristics when under stress. The relative importance of these phases of different elasticities varies during extension causing marked changes in the relationship between stress and strain. Although the nature of these changes is still largely unknown, their presence and location may be detected easily on the average load-extension curve. They occur at about 2 to 3% and 25 to 30% extensions, dividing the load-extension curve into three distinct regions.

Stress also results in dimensional distortion. The type of dimensional distortion is characteristic of the state in which the material exists and defines its basic physical characteristics. In semiliquids, only shape distortion occurs since the relative movement of the particles is free. However, in crystalline materials the displacement is restricted by molecular

[1] Contribution from the Division of Animal Husbandry, Experimental Farms Service.

forces, and shape distortion is accompanied by volume distortion. Thus, the problem arises as to whether differences in the stress-strain relationship in wool, as exhibited by the load-elongation curve, are accompanied by alterations in the type of dimensional changes. An answer to this question is important since it has a direct bearing on the interpretation of the elongation mechanism itself.

Generally, elongation is considered as a purely molecular phenomenon resulting from the "mechanical denaturation" of the folded peptide chains. However, it has been pointed out that in a material of such complexity as wool, where associations of an order higher than purely micellar exist, the tensile properties cannot be regarded as simple reflections of the base material behavior. Consequently, increased attention has been given to extramolecular phenomena involving the microfibrils and fibrils [7], stressing the morphological aspects of fiber extension.

The knowledge of dimensional changes is also helpful in assessing the proper relationship between stress and strain in view of the gradual decrease of the fiber cross-sectional area during extension.

With these implications in mind the present study was undertaken to determine the nature of the dimensional changes in wool fibers when extended from the decrimped state up to break. In addition to the main objective of the study, the method employed also permitted the collection of information on the decrease of the fiber diameter during decrimping, and the occurrence of mechanical damage in wool fibers owing to stress.

Materials and Methods

The wool fibers used in this study were obtained from the side wool of fine- and medium-woolled breeding ewes and rams. Small strands of wool were separated from the staples and cleaned by extraction first in ether, then in alcohol, for 24 hr. each, followed by rinsing in distilled water for 12 hr. The fibers were examined under a binocular microscope, and only those free from any apparent damage, free from medullation, having a low contour ratio, and showing uniformity of fiber thickness throughout the length were used. Fifteen fibers were selected for analysis.

The midsection of each fiber, 25 mm. in length, was mounted between the jaws of a specially designed instrument. For mounting the fibers a mixture of beeswax and colophonium was used, as slippage in this medium is negligible. The fibers then were elongated slowly by manual separation of the jaws. Measurements on the freely extended fibers were taken in the crimped state, the decrimped state, at 3, 5, 15, 20, 25%, etc., extensions up to break. After rupture the fibers were allowed to recover for 24 hr. after which the recovered diameters and the diameters of the broken ends in situ were determined. An effort was made to maintain standard atmospheric conditions (70° F. and 65% R.H.) during the entire experiment. However, the temperature ranged at times from 68° to 76° F. Slight variations in the temperature are known to have a negligible effect on the absorption of water vapor [9] and consequently would have little effect on these results.

Microscopic measurements were made with an ocular screw micrometer at a magnification of 440 ×. To minimize errors in the measurements, and those introduced by fiber nonuniformity, fiber ellipticity, and scale surface structure, the following precautions were taken.

1. All measurements were made by one operator.
2. The 25-mm. lengths under study were divided into segments 5 mm. in length by nylon knots as markers. This enabled the operator to space the measurements evenly throughout the length, thus counterbalancing errors introduced by the nonuniformity of fibers. Since the distances between the knots were known, the subdivision of fibers proved to be useful in obtaining data about the relative rate of extension of the subsequent fiber segments (reported elsewhere).
3. All measurements were taken immediately behind the upper scale edges.

The slight ellipticity of the fiber contours did not offer any serious difficulty. In a fiber with no twist at all; i.e., where the plane of the major axis remains unchanged along the whole length, as in human hair, fiber ellipticity may, and in most cases will, result in erroneous data. During this work it was observed that in human hair under stress, a slight rotation of the fiber axis often occurs. Measurements at different levels of extension, therefore, refer to different planes and consequently are not comparable. However, the natural twist always present in wool fibers will eliminate any serious error resulting from fiber ellipticity.

In each fiber 100 individual one-plane measurements were taken at each extension level, and the

average was considered as the diameter of a circle having the same area as the average cross-sectional area of the fiber.

Through a rigid observation of the above conditions, a high degree of accuracy could be maintained. Since the measurements had a precision of 0.1 mm. for length and 0.02 microns for diameter, the maximum error for fiber volume in the crimped state attributable to the measurements was calculated as follows:

$$\frac{\pi}{4}(D \pm 0.02\,\mu)^2(L \pm 0.1 \text{ mm.}) = V \pm \text{error}$$

and was found to be $\pm 76 \times 10^3$ microns^3, whereas the average of the deviations between fiber volumes at consecutive elongation levels was no more than $\pm 99 \times 10^3$ microns^3.

It should be pointed out that the experimental setup permitted only a very slow rate of extension over several days. However, this was not expected to affect the results appreciably. Speakman (as cited by Barker [2]) demonstrated that a slow rate of extension over a period of two weeks resulted in a typical curve.

Wherever possible, the data were tested for statistical significance by the paired-data treatment as described by Goulden [8].

Results and Discussion

1. Dimensional Changes during Decrimping

Evans and Montgomery [6] noted that the wool fiber exhibits a greater resistance to decrimping than to extension. Consequently, the regions of decrimping and the initial portion of the low-extension region in a load-extension curve are blended together. This feature renders impossible the accurate determination of the amount of length contraction resulting from the presence of crimp, since the length of the fiber at zero load is an indefinite quantity.

An attempt was made in this study to determine the crimped length. (Here the expression crimped length is used to denote the actual or "running length" of the fiber in its original crimped state.) The average diameters of the fibers studied were determined in both the crimped and decrimped state according to the method described earlier. The fibers were regarded as "decrimped" when the deviations from the straight lines representing the outlines of the fibers became less than about half the fiber thickness. The degree of decrimping was checked under the microscope at a magnification of 150 ×. Comparison of the paired data showed that decrimping resulted in a decrease of 0.38 micron or 1.2% ($P < .01$) of the fiber diameter.

The length contraction due to crimp may be calculated if the Poisson's ratio (σ) is known. The Poisson's ratio had a value of about $\sigma = 0.63$ (see Section 4) in the initial portion of the curve. Assuming that the elastic properties remain unchanged in the entire Hookean region, the amount of contraction is obtained by the equation

$$\Delta L = \frac{L_d\,\Delta D}{\sigma D_d}$$

where ΔL = contraction in length due to crimp, L_d = decrimped length of the fiber, D_d = diameter of the decrimped fiber, ΔD = lateral contraction due to decrimping, and σ = Poisson's ratio. Substituting the average values as obtained in this study ($L_d = 25.09$ mm., $D_d = 25.99\,\mu$, $\Delta D = 0.38\,\mu$, $\sigma = 0.63$), the average contraction in length due to crimp was found to be 0.58 mm. or 2.3% as related to the decrimped fiber length.

It was reported recently that extension in the initial portion of the load-extension curve is closely associated with the degree of crimpiness [5, 10]. Wyk and Venter [15] further pointed out that both fiber diameter and crimp level are determining factors, and thus the initial extension in fact depends on the relationship of diameter and crimp. Since, in this respect, considerable variation exists, no definite trend can be expected. In this study a correlation coefficient of -0.504 was obtained between fiber diameter and relative decrease of the fiber diameter during decrimping among the fibers from ewes. This, however, decreased to -0.126 if the data of ewes and rams were combined. Neither of these coefficients was significant.

2. The Rate of Lateral Contraction in Fibers under Stress

During the stretching process a progressive decrease in the fiber diameter occurs. Since, in this study, there was a considerable variation in the initial diameters of the fibers, the decrease was expressed as a ratio of the initial diameter. The relative diameter changes ($\Delta D/D_d$) thus obtained were averaged and plotted against the respective relative length changes ($\Delta L/L_d$). The plot is shown in Figure 1. For the purpose of comparison, Figure 1 also contains the plot denoting the relative rate of decrease in the fiber diameter assuming that no vol-

ume change takes place during extension. In this case the square of the ratio of the original diameter to the decreased diameter is equal to the inverse ratio of the respective fiber lengths.

$$\frac{D_d^2}{D^2} = \frac{L}{L_d}$$

Since $D = D_d - \Delta D$, and $L = L_d + \Delta L$, the ratios $\Delta D/D_d$ may be calculated for the different extension levels (the negative sign denotes that in extension $\Delta D/D_d$ is a negative quantity).

$$-\frac{\Delta D}{D_d} = 1 - \frac{1}{\sqrt{1 + \frac{\Delta L}{L_d}}}$$

If this equation is expressed in the form of an infinite series,

$$-\frac{\Delta D}{D} = \frac{1}{2}\frac{\Delta L}{L_d} - \frac{3}{8}\left(\frac{\Delta L}{L_d}\right)^2 + \frac{5}{16}\left(\frac{\Delta L}{L_d}\right)^3 - \cdots + \cdots \text{etc.}$$

it becomes obvious that constant volume distortion can be described by a parabolic function if the changes are not too large. Accordingly, the data obtained in this study were fitted to the following equation employing the method of least squares.

$$y = +ax - bx^2$$

By using a third- or fourth-degree function, a slightly improved fit could be obtained. However, for computational reasons only the first two terms were assumed to have real significance. For the same reason the slight but significant deviations at the 0 to 2.9% and 24.2 to 28.4% extension levels also were neglected. The resulting curve expresses the following relationship.

$$\frac{\Delta D}{D_d} = -0.5862\,\frac{\Delta L}{L_d} + 0.5532\left(\frac{\Delta L}{L_d}\right)^2$$

and is shown in Figure 1.

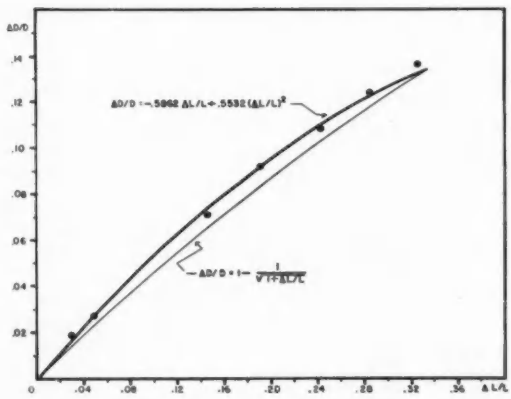

Fig. 1. Relative diameter change ($\Delta D/D_d$) of wool fiber resulting from tensile stress plotted against the relative increase in length ($\Delta L/L_d$). (Basis: decrimped length.)

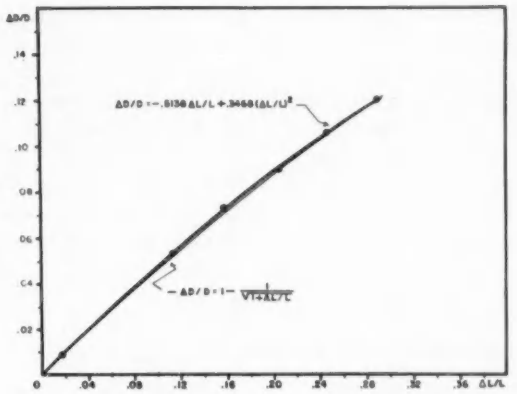

Fig. 2. Relative diameter change ($\Delta D/D_{2.9}$) of wool fiber resulting from tensile stress plotted against the relative increase in length ($\Delta L/L_{2.9}$). (Basis: length at 2.9% extension.)

The deviations between the empirical and theoretical curves are due mainly to the fact that during the Hookean extension the fiber exhibits a marked decrease in volume. If the data relating to the initial phase of extension are omitted, and only those beyond the 2.9% extension level are used, the differences become negligible. The regression equation then takes the following form.

$$\frac{\Delta D}{D_d} = -0.5138\,\frac{\Delta L}{L_d} + 0.3468\left(\frac{\Delta L}{L_d}\right)^2$$

with constants equal within precision of measurement to those of the theoretical equation (Fig. 2).

It is therefore concluded that in wool fibers under stress an essentially constant volume distortion takes place beyond the Hookean extension.

Fiber breakage is associated with a pronounced decrease in the fiber diameter. Sadykova [12] reported that fiber breakage occurred when the lateral contraction was about 15%. In this experiment the average contraction at the extension level before break was 13.1% (7.4 to 17.2%). However, these values mean little unless the degree of lateral contraction at break is uniform along the entire fiber length. Since wool fibers elongate differentially [1], this is obviously not the case. The fibers used in

this study were measured in the recovered state 24 hr. after rupture. At the same time the diameters of the broken ends in situ also were determined. The data were analyzed by the paired treatment, and it was found that the average cross-sectional area of the broken ends was 32% smaller ($P < 0.01$) than the average for the entire fiber. This is considered as further indication that under normal conditions (i.e., in sound, undamaged fibers) maximum extension resulting in rupture usually will occur at the thinnest segment. The actual decrease in diameter associated with break is therefore probably of a much higher order than indicated by Sadykova.

3. Volume Distortion in Fibers under Stress

The relative decrease in fiber diameter at different extension levels has indicated that the over-all trend, at least beyond the Hookean region, is a constant volume distortion. However, slight deviations were observed at different extension levels. To test whether or not these deviations were real, the volumes of the fibers were calculated, and the significance of differences between individual values at subsequent elongation levels estimated. A direct comparison of the averages was not possible because rupture occurred at different extensions. The deviations, together with their probabilities, are listed in Table I.

A significant decrease ($P < 0.05$) in volume occurred while the fiber was extended from the decrimped state up to 2.9% of its length. Also, a significant volume increase became evident at about 24% elongation. It was shown earlier that decrimping was associated with an extension of about 2.3%. Consequently, the above deviations, suggesting some drastic structural changes in the wool substance, occurred in fact at about 5 and 27% extensions, respectively.

TABLE I. Volume Changes of Wool Fibers at Subsequent Extension Levels

Extension level (%)	Average difference in volume μ^3 ($\times 10^3$)	Probability	
0– 2.9	−156	<0.05	>0.01
2.9– 4.8	0		
4.8–14.6	−42		>0.05
14.6–19.2	−2		>0.05
19.2–24.2	+129	<0.05	>0.01
24.2–28.4	+11		>0.05
28.4–32.4	+49		>0.05

TABLE II. The Average Poisson's Ratios of the Wool Fiber at Different Levels of Extension

Extension level (%)	Poisson's ratio
0– 2.9	0.63
0– 4.8	0.56
0–14.6	0.48
0–19.2	0.48
0–24.2	0.45
0–28.4	0.44
0–32.4	0.42

While this work was in progress, Bull [3] published data regarding changes in the elastic properties in human hair under stress. Employing essentially the same technique, he found a marked volume decrease in the Hookean region, whereas the maximum volume was reached at about 30% extension. This is in general agreement with the present findings. He also noted that, after the Hookean extension was completed, a steady volume increase took place in human hair up to 30% extension, but thereafter the volume decreased. In the present study on wool, no such trend was observed.

It was reported elsewhere [1] that the subsequent segments in a wool fiber will extend differentially if stress is applied. These differences were found to be correlated to the average cross-sectional area of the respective segments and could be explained on the basis of fiber nonuniformity. The phenomenon of differential elongation imposes some limitations upon the applicability of results as obtained by the outlined procedure concerning dimensional changes in wool fibers. In a filament of nonuniform cross section such as wool, the different portions of the fiber may be at different stages of elongation causing an overlapping of the Hookean yield, and postyield regions, respectively, of the force elongation curve. Consequently, the loci of inversion may be shifted considerably according to the degree of nonuniformity. This in turn means that eventual volume changes are distributed over a range and therefore are less pronounced.

4. The Poisson's Ratio

In a nonhomogeneous and nonisotropic material such as wool, the elastic properties vary considerably in different directions. The method employed in this study permitted only the determination of the rate of lateral contraction in relation to the relative extension at subsequent extension levels. These ratios (Poisson's ratios) were calculated (Table II)

and plotted against the relative length change (Figure 3). It will be noted that constant volume distortion is characterized by a ratio of $\sigma = 0.5$. Significantly smaller or greater values than $\sigma = 0.5$ are the results of volume increase or volume decrease, respectively.

The asymptotic character of the resulting curve is due mainly to the fact that at the beginning of the extension a marked volume decrease took place. If we disregard these high initial ratios and the remaining ratios are calculated from the 4.9% extension level as basis, only a slight skewness remains which may be satisfactorily explained by the variations encountered. The ratios approach constancy with an estimated average value of 0.46.

The actual diameter of the wool fiber at any chosen extension level may be determined using the following formula.

$$D_x = D_d \left[1 - \sigma \left(\frac{L_x}{L_d} - 1 \right) \right]$$

where

D_d = average diameter of the decrimped fiber
L_d = length of the decrimped fiber
σ = Poisson's ratio

Warbourton [13, 14], employing the method of Cornu, obtained ratios of 0.24 and 0.33 on horn keratin. However, his data refer to the rate of contraction in the tangential direction, whereas here the rate of transverse contraction was measured. Since his values and those obtained in this study refer to different axes of symmetry, no comparison is attempted.

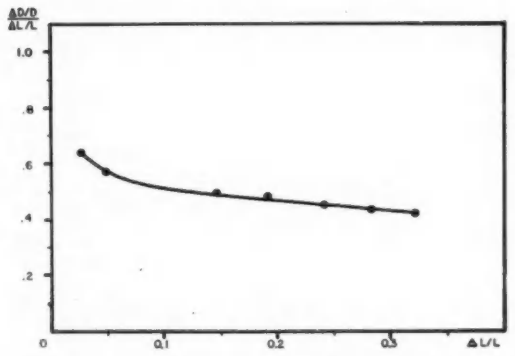

Fig. 3. The Poisson's ratios of wool fibers as plotted against the relative change in length. (Basis: decrimped length.)

5. The Occurrence of Mechanical Damage during Elongation

Reumuth [11] reported extensive mechanical damage when wool fibers were looped together and stretched. The cuticle became loose from the underlying elements, slipped back in a sleevelike fashion, and the cortex split. The author considered this to be evidence of differences in the elastic constants of the various structural elements. A similar observation was made by Bull [3] on human hair. Bull observed a shearing of the cuticle between 40 and 60% extensions.

During this study the fibers were checked throughout their entire length at each extension level up to break, and after rupture in the recovered state for possible damage. Extensions as related to the total length ranged from 14.0 to 33.3% As pointed out earlier, because of the differential elongation, the extension of the subsequent fiber segments was unequal. The method employed did not permit the measurement of the actual extension occurring at the thinnest segment immediately before rupture, but evidence was obtained that it is of much higher order than the values generally described as "breaking extensions" related to the total length. Since the rate of separation of the cuticular cell boundaries is greater in these portions, the thinnest segments, showing maximum extension, could be easily recognized under the microscope. Although particular attention was given to these portions, no visible damage to any of the structural elements could be observed within the extensions encountered. It seems probable, therefore, that the damage noted by Reumuth in looped fibers resulted from a shearing effect rather than from differences in the elastic properties.

It is of interest to mention that in two cases the rupture of the fibers took place several hours after they had been subjected to the required extensions. Since the possibility of an external force causing rupture is out of the question for this rather puzzling phenomenon, the following explanation is suggested. Cruise [4] observed recently that stresses set up in some textile fibers by impact propagate in a wavelike fashion. The damping of these stress fringes required considerable time. Because of the internal structure of the wool fiber, it is possible that stresses set up by loading are not uniformly distributed and that a considerable time will elapse before they are levelled out. During this process the

stress related to the thinnest segment of the fiber may increase sufficiently to cause rupture.

Summary and Conclusions

Fifteen wool fibers ranging in thickness from 20.9 to 34.4 microns were measured throughout different stages of their elongation up to break employing the standard optical method. Transverse and longitudinal measurements were used to determine the type and magnitude of dimensional changes occurring in wool under stress.

The main results of this investigation are as follow:

1. Decrimping was associated with a significant decrease (1.2% with $P < 0.01$) in fiber diameter. The amount of longitudinal contraction due to crimp was calculated to be 2.3% of the decrimped fiber length.

2. The over-all rate of decrease in the fiber diameter as related to the rate of extension indicated a constant volume distortion beyond the Hookean extension in wool fibers when stretched. However, slight but significant ($P < 0.05$) deviations from the general trend at about 5 and 27% extensions suggested the possibility of drastic structural changes at these levels within the fiber substance.

3. The Poisson's ratio (denoting here the rate of lateral contraction to the rate of length increase) was found to have a value of 0.63 in the region of the Hookean extension, whereas in the later stages of the extension it approached a value of 0.46.

4. Rupture occurred at the point where the cross-sectional area was on the average about ⅓ smaller ($P < 0.01$) than the average cross-sectional area of the entire fiber.

5. Extension did not cause visible mechanical damage to any of the structural elements within extensions ranging from 14.0 to 33.3%.

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Literature Cited

1. Banky, E. C., and Slen, S. B., TEXTILE RESEARCH JOURNAL **25**, 358 (1955).
2. Barker, S. G., *Wool Quality*, H. M. Stationery Office, London, p. 242 (1931).
3. Bull, H. B., *J. Phys. Chem.* **58**, 101 (1954).
4. Cruise, A. J., *Nature*, 4437, 923 (1954).
5. Evans, T. F., TEXTILE RESEARCH JOURNAL **24**, 639 (1954).
6. Evans, T. F., and Montgomery, D. J., TEXTILE RESEARCH JOURNAL **23**, 689 (1953).
7. Fuhrmann, W., *Melliand Textilber.* **33**, 911 (1952).
8. Goulden, C. H., *Methods of Statistical Analysis*, 2d ed. John Wiley & Sons, Inc., New York, p. 55 (1952).
9. Lennox, F. G., *Australian Council Sci. Ind. Research*, Pamphlet 83 (1938).
10. O'Connell, R. A., and Yeiser, A. S., TEXTILE RESEARCH JOURNAL **24**, 629 (1954).
11. Reumuth, H., *Melliand Textilber.* **33**, 41 (1952).
12. Sadykova, F. K., *Texstil'naya Prom.* **11**, 29 (1951).
13. Warbourton, F. L., personal communication, 1954.
14. Warbourton, F. L., *J. Textile Inst.* **39**, 297 (1948).
15. Wyk, C. M., and Venter, J. J., *J. Textile Inst.* **45**, T809 (1954).

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Performance Characteristics of Synthetic Fibers, Wool, Viscose, and Blended Fibers in Axminster Carpets[1]

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Abstract

The soiling and crushing characteristics of nylon, Dacron,[2] Orlon,[3] Saran, Dynel, acetate, wool, and smooth viscose, as well as the 50/50 blends of the synthetics and wool with smooth viscose were studied in Axminster carpets.

Soiling properties are shown to be related to the fiber surface smoothness and available surface area, and the reflective properties of the fiber. The soiling properties of fibers in blends are not influenced by the companion fibers of the blends. Electrostatic effects are unrelated to the soiling properties of carpet fibers.

Smooth viscose has the highest soil resistance of all the fibers appraised and contributes this property to carpets consisting of blends of smooth viscose and synthetics.

Crush recovery characteristics of the synthetics are good with nylon and Orlon performing better than wool. Blends of the synthetics and smooth viscose show poorer crush recovery than the average crush properties of the respective fibers.

Pile density is a variable controlling crush properties of carpets and varies in relation to the fiber's specific gravity. Differences in pile density of carpets as a result of differences in specific gravities of fibers are insufficient to materially shift the crush resistant rankings of the fibers.

I. Introduction

Until recent years, the carpet industry in this country has utilized carpet wools almost exclusively. Carpet wools have proved acceptable because they combine most of the desirable properties and few of the undesirable properties of carpet fibers. During the last decade and more specifically within the last several years, a definite trend away from wool and toward the utilization of man-made fibers has been evident.

This trend has not resulted from the ability of man-made fibers to out-point wool in every area of fiber performance, but rather from a combination of circumstances: (1) shortage of world wool supplies with resultant high prices, (2) development of new carpet manufacturing methods to which man-made fibers are readily adaptable, and (3) an understanding of fiber properties and development of methods for utilization of these properties.

The performance characteristics of wool in carpets should be considered in order that comparisons with other fibers may be made. Carpet people have recognized that the best carpet wools have excellent soil, crush, and abrasion resistance. Naturally, there are other qualifications for good performance of fibers in carpets, but the above-mentioned properties are considered to be paramount.

This paper will deal specifically with the soil- and crush-resistant properties of carpet fibers and will examine the performance of some of the better known synthetics, viscose, acetate, and wool fibers when utilized in carpets. These two properties, as related to carpets, may be defined as follows:

Soil resistance: The ability of a fiber to release street or household soils brought into contact with the fiber in service. Soil applied to the fiber in service should be removable by mechanical and vacuum devices.

Crush resistance: The ability of a fiber to store energy in deformation and release the energy through work in restoring the fiber to its initial geometry.

[1] A paper presented to the Fiber Society at Alabama Polytechnic Institute, May 4, 1955.

[2] Du Pont polyester fiber.

[3] Du Pont acrylic fiber.

Various investigators have examined the mechanisms of fabric soiling which may be summarized as follows as they apply to carpet soiling:

1. Mechanisms of impingement and retention [5] are operative in the soiling of textile fibers. By impingement, soil is brought into contact with the fiber through direct transfer and deposition as well as by inertial and diffusional movement of air-borne soil.

2. The mechanisms of retention [2] involve (*a*) macro-occlusion, or entrapment of particles in the intrayarn or interyarn spaces—filament denier size is a factor in interyarn entrapments, and (*b*) micro-occlusion, or entrapment of particles in the irregularities of the fiber surface.

3. Oil bonding [3, 15] is another important mechanism of soiling which describes the fixation of soil to a fiber through adhesion. The presence of oily fixative materials on carpet fibers is due to fiber processing lubricants, contaminants, and oils wicked from base fibers.

4. Electrostatic effects [13] have been mentioned as contributing to soiling although no conclusive evidence has been brought forward to prove the relationship to carpet soiling.

5. Available surface area [6] is a criteria of soiling and is related to the denier and cross-sectional shape of the fiber.

Of the above factors controlling the soiling of fibers, oil bonding is most readily controlled in the manufacture of the carpet. Soil fixation through micro-occlusion is a specific property associated with the morphology of the fiber and may be considered a primary soiling factor. When a carpet is soiled, mechanical forces press soil into the surface of the fiber, either into naturally occurring crevices, cracks, and pits, or into the smooth area of the fiber through indentation of the soil into deformable fiber surfaces.

The optical properties of a fiber [12, 14] control the apparent soiling to a significant degree since the apparent soiling is a function of the reflectivity characteristic of a fiber. Man-made fibers are controlled with respect to luster by the addition or deletion of delustrant pigments, the pigments acting as reflective surfaces in and on the fiber. Two fibers having equal soil retention properties but unlike in respect to luster will appear to soil differently; the dull fiber reflecting more light than the bright fiber and consequently appearing cleaner.

Investigation of the resistance to crushing of carpet fibers is considered exceedingly complex. The factors which control the crush resistance of a carpet may be considered in two phases: (1) the physical properties of the pile fibers and (2) the carpet construction. The analysis of the importance of the two factors is complex, and investigators have only pointed to the interrelationship of the factors. Obviously, carpet construction can be eliminated as a variable in fiber comparisons, and differences in crush resistance become functions of the fiber properties.

In the consideration of carpet fiber properties which affect the crush resistance or recovery, attention must be given to fiber denier, stiffness, elastic recovery, interfiber friction, and moisture regain. As the denier of a fiber is increased, its stiffness and resistance to bending becomes greater. Since carpet fibers undergo bending as a result of compressional forces, opposite forces of tension and compression occur in the same fiber, and the tensional elongation and the compressional deformation vary as a function of the fiber diameter. Several investigators have shown some correlation of elastic recovery properties of fibers in tension with recovery of pile fabrics subjected to crushing.

Interfiber friction is an unknown quantity in carpet-fiber crush recovery. Measurement of frictional properties of clean fiber offers no problem, and it is readily seen that the ability of fibers to work with minimal friction effects will affect recovery properties. Nevertheless, since soil is accumulated by carpets in service and each fiber has different soiling properties, the effect of soil on interfiber friction cannot be overlooked.

Moisture regain of fibers and water sensitivity are important criteria of crush recovery. Sayre and Weldon [11] have shown poor crease recovery of rayon fabrics to be attributed to their high moisture regain and high water swelling. Fibers with high moisture regain may be described as being subject to hydroplasticity. Cellulosic fibers are marked by high regain properties. When these fibers are stressed, hydrogen bonds may be broken and re-established in the strained state, thereby fixing the strained conditions and retarding the recovery of the fiber.

II. Carpet Testing Program

The purpose of this study was to determine the performance of some of the better known synthetic fibers, wool, viscose, acetate, and 50/50 blends of synthetics/viscose and wool/viscose when utilized in

carpet. The interest in investigating blends of wool or synthetics with viscose is purely economic, in that carpet manufacturers are seeking relatively low cost fibers with satisfactory performance properties. Studies of the fibers were made in the laboratory in an effort to understand the soiling and crushing characteristics. Service tests of the respective fibers and blends in carpets permitted correlations to be made with the fiber studies.

It appeared desirable when programming the study to include a wide range of synthetic fibers, but it was realized that several synthetic fibers were not produced in deniers considered most desirable for carpets. Therefore, fibers varying in denier from 6 to 24 den./filament were included in the study, and conclusions based on comparisons of these fibers must be qualified.

Tables I and II list the types and specifications of fibers used in this study. It will be noted that a letter code is used to designate a particular fiber, and this code will be followed in the description of fibers in the graphs which will follow. The luster of the fibers used in the tests are either bright or dull for the synthetics, the viscose and acetate being dull. In the case of the viscose, a smooth type, round cross-section carpet fiber was used, primarily because of its known soil resistance.

For the service testing, the various fibers and blends were processed on the woolen system into 1.08/2, 4.25 T.Z., 1.8 T.S. plied yarn. Because of difficulties in spinning, the Saran fiber was processed on the worsted system and to the same construction. Two other exceptions to the yarn construction were made in order to appraise the factor of fiber specific gravity as it relates to carpet-pile fiber density and crushing; a viscose yarn of 0.93/2 ply and a nylon yarn of 1.24/2 ply, woolen run, were spun for this purpose.

Processing of the fibers into yarn required lubrication in carding and, in most cases, water was the only lubricant.

TABLE I. Fiber Specifications

Code	Description
V	15.0-den., 3-in. dull smooth viscose
W	Wool, 20% B.A.'s, 40% white Awassi, 40% white Vicanere
AC	17.0-den., 3-in. dull acetate
N	15.0-den., 3-in. bright nylon, type 100
N-6	6.0-den., 4-in. dull nylon
D	6.0-den., 2½-in. bright Dacron
OR	6.0-den., 3-in. bright Orlon
S-22	22.0-den., 3-in. dull Saran
DY	24.0-den., 3-in. bright Dynel

TABLE II. Fiber Blend Specifications

Code	Description
V/W	50% 15-den., dull smooth viscose/50% wool
V/N	50% 15-den., dull smooth viscose/50% 15-den., bright nylon
V/OR	50% 15-den., dull smooth viscose/50% 6-den., bright Orlon
V/D	50% 15-den., dull smooth viscose/50% 6-den., bright Dacron
V/DY	50% 15-den., dull smooth viscose/50% 24-den., bright Dynel

The yarns were processed in their natural color into a standard 7-row Axminster fabric, 5/16-in. pile height, with a jute filling yarn having a nonmigratory finish. The carpets were given a standard carpet finishing and finally were subjected to a Naphtha dry cleaning for the purpose of removing producer finishes, processing finishes, and yarn contaminants which could materially influence the soiling and crushing behavior.

A. Service Testing

Carpet samples measuring $27 \times 13\frac{1}{2}$ in. were service tested in the R.D.D. laboratory corridors of American Viscose Corporation at Marcus Hook, Pa. The samples were vacuum cleaned daily and rotated weekly in order to obtain a statistically random order of service testing. The carpets were service tested for an 8-week period, or for 20,000 footsteps, at a rate of approximately 500 footsteps per 8-hr. day.

During the service test period, the carpets were systematically checked with measurements of soiling and crushing being made at regular intervals.

B. Measurement of Soiling

Reflectance measurements were made with a Photovolt Reflectometer, Model 610, using a green filter. A double-thickness window glass, 3×3 in., was placed on the carpet surface, and the search unit was centered on the glass plate. A pressure of 20 lb. was applied to the search unit to eliminate differences in texture which can markedly affect the reflectance readings. Reflectance readings confined to the central area of the carpet were taken on each sample for each period of testing.

Since the carpets were undyed and the fibers appeared in their natural color, the wide range in original reflectances made comparisons of soiling differences difficult. Comparisons of reflectances either directly or by differences between original and soiled values did not correlate with observed visual differences. The Kubelka-Munk equation, $K/S = (1 - R)^2/2R$, in which K is the coefficient

of light absorption, S is the scattering coefficient, and R is the reflectance, has been used by a number of investigators [1, 4, 9, 14] to relate reflectance readings to the soil content of a fiber. Although it is recognized that the expression is not useful in comparing the soil contents of different fibers, the reflectance relationships as given in this expression are useful in comparing the appearance changes due to soiling of different fibers. For the purpose of this study, the different fibers were appraised for soiling by measuring the appearance change or "apparent soil" which is defined as

$$\text{Apparent soil} = \frac{(1 - R^1)^2}{2R^1} - \frac{(1 - R)^2}{2R}$$

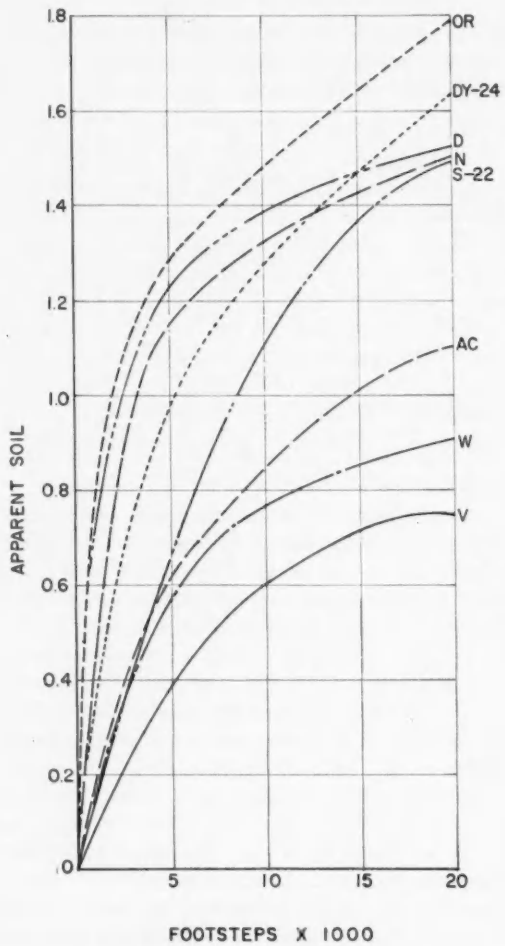

Fig. 1. Soiling characteristics of synthetic fibers, viscose, acetate, and wool.

where R = unsoiled fiber reflectance and R^1 = soiled fiber reflectance.

It should be understood that apparent soil is not to be construed as soil content in the comparison of the different fibers.

C. Measurements of Carpet Crushing

The crushing of a carpet in service is marked by two effects: (1) the loss in thickness of the carpet and (2) the loss in compressional deformation under loading. Loss in thickness may be readily determined by measurements of thickness of loads of 0.1 lb./in.^{2} at periodic intervals during the service testing period. This measurement correlates with the change in appearance and texture as observed by the eye and permits the grading of carpet where the differences in thicknesses are small.

Loss in compressional deformation [8] under loading is equivalent to the loss in luxury "feel" of the carpet. High compressional deformation of a carpet is desirable since it gives feeling of luxury underfoot. For fabrics of similar construction, therefore, the decrease in thickness under a similar increment of load may be considered a measure of their ability to absorb energy, or in other words, a measure of their compressibility. Therefore, the measuring of the residual compressibility of a sample which has been in service, provides a means for evaluating its resistance to crushing.

Residual compressibility of a carpet fabric was measured by determining the difference in thickness of the carpet at 1.27 and 11.5 lb./in.^{2} at various stages during the service test period as the carpet approached an equilibrium condition of crushing.

Measurements of carpet thicknesses were made with a compressometer designed to apply loads of 0.1, 1.27, and 11.5 lb./in.^{2} The carpet samples were tested before service testing and at intervals of 5000 footsteps.

III. Service Test Results

The following illustrations permit a graphic representation of the soiling and crushing characteristics of the various carpet fibers and blends in Axminster carpets. In Figure 1, a plot of the apparent soil versus footsteps or service is presented. It will be noted that the smooth viscose exhibits best soil resistance with wool and acetate following in that order. The true synthetic fibers show a marked increase in rate and severity of apparent soiling. The various synthetic fibers show real differences

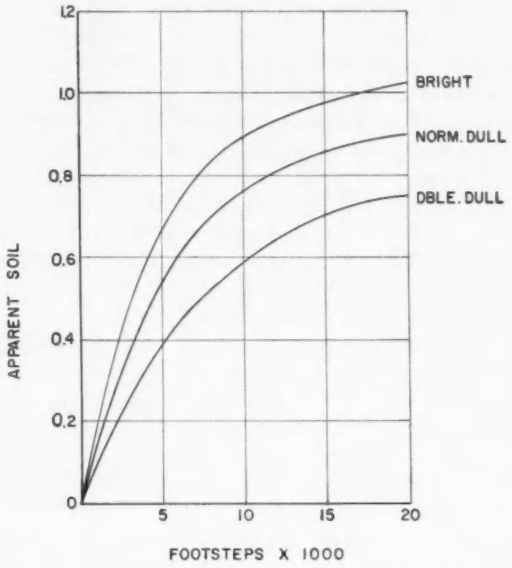

Fig. 2. Soiling characteristics of 15-den. smooth viscose fibers varying in delustrant content.

in rate of soil but only slight differences in degree of soil. The lowest soiling synthetic, Saran 22, is not appreciably better than Orlon which exhibits the highest soiling degree. Although the synthetics as a group have fiber denier variation of 6 to 24, the apparent soiling of the carpets is not dissimilar.

The luster characteristics of a fiber, i.e., its dullness or brightness, controls its ability to reflect light and is of utmost importance in comparing soilability of fibers. In this study, it was not possible to obtain the various fibers in a wide range of lusters. Many of the synthetics were only obtainable in bright lusters which accentuate the soiled appearance of the fiber. Figure 2 illustrates the differences in apparent soiling of viscose fibers having luster variation from full dull to bright. The fiber identifications refer to the delustrant concentration, bright = O% TiO_2, normal dull = 0.75% TiO_2, and double dull = 1.50% TiO_2. A marked improvement in apparent soil resistance is shown for the double dull viscose although the amount of soil present on all three fiber types is identical.

Since comparisons of dull and bright fibers are being made in this study, it is necessary to bear in mind the need for adjustment of bright fiber reflectances if a critical comparison is to be made. Such adjustments cannot be calculated or arrived at arbitrarily, but must be based on specific dull and bright fiber comparisons. The relationship of apparent soiling to the specific soiling property will be considered in the laboratory appraisal of the fibers.

The soiling properties of the 50/50 blends of the synthetics and wool with smooth viscose is graphically presented in Figure 3. These graphs illustrate the soiling characteristics of wool, nylon, Orlon, and Dynel blended with viscose. The soil characteristics of the component fibers are also plotted to permit comparisons. It is noted that the 50/50 blends soil equivalent to the average of the soiling properties of the component fibers. Therefore, it is concluded that specific fibers in blends soil at the same rate and to the same extent as fibers present in carpets in 100% form.

The effect of static electricity on the soiling properties of carpets has been considered by several investigators. Firm conclusions as to its effect on carpet soiling have not been reported, and it was considered worth while to determine if soiling behavior correlated with electrostatic properties of the carpets.

In order to make the correlation, it was necessary to measure the characteristics of the carpet samples to acquire a static charge as well as the tendency to dissipate the charge. The various carpet samples were studied for electrostatic properties by mounting samples on the periphery of a drum, permitting the sample to be rotated in contact with a polyethylene shoe. Measurement of static by inductance was made with a Keithley high input impedance electrometer. All measurements were made at 30% R.H.

TABLE III. Electrostatic Properties of Axminster Carpets at 30% R.H. Synthetics, Viscose, and Blends

Fiber	Charge	Decay
Viscose	v.s.	—
Wool	v.h.	slow
Acetate	v.h.	very slow
Nylon	v.h.	very slow
Dacron	h.	very slow
Orlon	v.h.	very slow
Saran	h.	very slow
Dynel	s.	—
Viscose/wool	m.	slow
Viscose/nylon	s.	—
Viscose/Dacron	m.	—
Viscose/Orlon	v.s.	—
Viscose/Saran	s.	fast
Viscose/Dynel	v.s.	—

v.s. = <5 volts; s. = <10 volts; m. = 10 to 20 volts; h. = 20 to 30 volts; v.h. = very high.

In Table III, electrostatic data for the samples are tabulated. The electrostatic charge is graded in voltage steps of very slight charge for < 5 volts; slight charge for < 10 volts; medium charge for 10 to 20 volts; high charge for 20 to 30 volts; and very high for 30 volts. Although this grading lacks high precision, it is considered satisfactory for the relative grading of carpets.

Viscose is the only fiber rated as having a slight charge, most of the synthetics, wool, and acetate being rated as high or very high in charge. The decay rate is called "very fast" if the RC[3] constant is in the order of 1 min.; "fast" for minutes; "slow" for 1 hr. Although most of the synthetic fibers show a high static charge and high soilability, a relationship between high static-charge properties and soilability does not appear. Wool also acquires a high static charge and has a low soiling level. Dynel shows only a slight charge but soils to a high degree.

The clue to the effect of static on soiling may be gained from examination of some of the viscose/synthetic blend properties. Blends of viscose/nylon, and viscose/Saran have only slight static charge, indicating the ability of the viscose to nullify the tendency of the synthetic to acquire a charge. Soiling properties of these blends, as previously discussed, reflect the proportional soiling characteristics of the fiber components, or, in other words, the nylon and viscose fibers soil at the same rate and to the same extent as if the companion fiber of the blend were absent. Since the electrostatic properties of the blend are entirely different from either the nylon or viscose carpet, electrostatic effects in soiling are considered to be minimal or nonexistant.

In the service crush tests of the various fibers and blends, the carpets were tested for the pile thickness retention and the residual compression. Figure 4 presents the crush performance of the fibers, plotting per cent of pile-thickness retention at 0.1 lb./in.^{2} versus footsteps or service. Here it is noted that the synthetics have much better crush resistance than viscose and acetate. Nylon and Orlon have better crush resistance than the wool carpet blend. Dynel is equivalent to wool, and Dacron and Saran are slightly inferior. The graphs illustrate that rate of loss of pile thickness for viscose is exceedingly high for the initial service period and then levels off.

[3] RC constant is the time required for a capacitor to discharge to $1/e$ its former value.

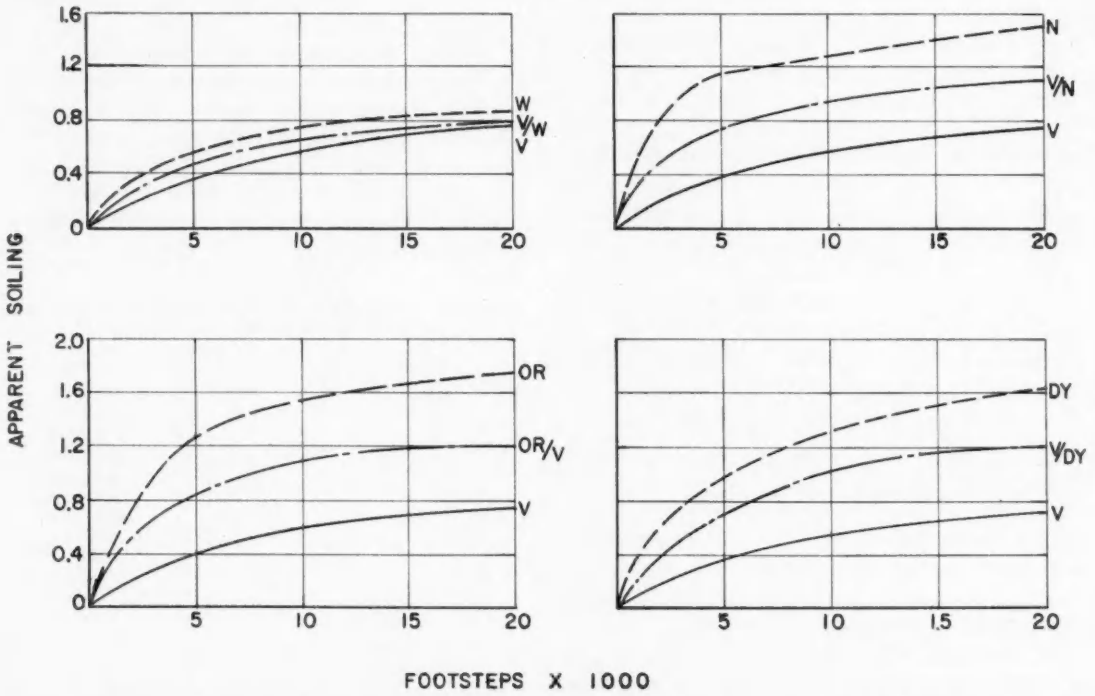

Fig. 3. Comparison of the soiling characteristics of blends of synthetic fibers and wool with viscose.

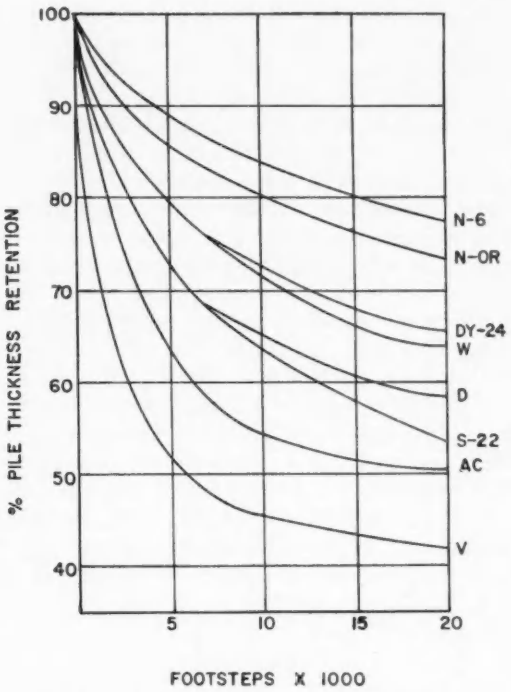

Fig. 4. Thickness retention characteristics of synthetic, viscose, acetate, and wool carpets.

Figure 5 shows the per cent of pile-thickness retention relationship of the 50/50 blends of wool, nylon, Orlon, and Dacron with viscose. Although the blends exhibit crush-recovery properties related to the properties of the component fibers, the blends fail to equal the average of the component fiber properties. In each fiber blend, the performance characteristic is less than the average of the components, with wool giving least support to the viscose. The nylon, Orlon, and Dacron fibers blended with viscose yield better crush-recovery properties than the wool blend. Selection of better carpet wools could change the picture, but the wools used in this study represent a carpet fiber blend chosen to be representative of present-day blends.

Residual compression tests made on the carpets in service test are presented graphically in Figure 6. The difference in thickness between loadings of 1.27 and 11.5 lb./in.^{2}, or the residual compression, is plotted against footsteps or service. It is noted that viscose and Dacron carpets have very high initial values which reflect higher stiffness of the fibers. As the viscose is subjected to service, its loss in residual compression is severe. The synthetic fibers and acetate exhibit similar rate losses apparent in the parallel curves. Nylon, wool, and Dacron excel in residual compression, with acetate and viscose showing poorest performance. Saran occupies a low position in the series of curves, but this is explained on the basis of a thermal shrinkage of the pile in carpet finishing resulting in abnormally low pile height and consequently a low residual compression.

Figure 7 illustrates residual compression performance characteristics of the wool and synthetic blends with viscose. These curves correlate well with the pile-thickness retention characteristics for the blends; the blend behaving inferiorly to the anticipated average residual compression of the component fibers.

The crushing of a carpet is affected by the pile density or the total cross-sectional fiber area per unit area of carpet. It is obvious that a high pile-density fabric will resist crushing to a greater extent than a low pile-density fabric. By the same token, if yarns having equal weight but unlike fibers are appraised in carpets, the fiber having the highest specific gravity will have the lowest pile density. Hence, it might be anticipated that comparison of viscose with nylon in carpets having similar pile weight would present the higher specific gravity fiber, viscose, to disadvantage. In order to check this finding, nylon yarns of run 1.08/2 ply and 1.24/2 ply and viscose yarns of run 0.93/2 ply and 1.08/2 ply were tested in carpets of similar row, pitch, and pile-height construction. The 0.93/2-ply viscose is equivalent to 1.24/2-ply nylon. Figure 8 gives a comparison of the crush-resistance properties of carpets constructed from these yarns. It is readily seen that although improved crush recovery is found with the higher pile density for a given fiber, the correction for pile density does not change the relative performance of the nylon and viscose.

IV. Laboratory Appraisals of Carpet Fibers

Service testing of carpets presents the picture of carpet fiber performance in an indisputable manner, but unfortunately it does not always permit an understanding of the fiber behavior. In order to gain a fuller understanding of soiling and crushing characteristics, laboratory examinations of the fibers were made.

A. Soiling

In the appraisal of soiling, the fibers were tested by accelerated soiling procedures, tested for actual

soil pickup, and examined microscopically to determine the soiling proclivities of the fiber.

Laboratory soiling techniques require a soil of uniform chemical composition and particle size. Synthetic soils fill the basic requirements for soil, and the composition recommended by Sanders and Lambert [10] was used in all laboratory investigations. The composition of this soil will not be detailed since it has received wide publicity, except to point out that it is basically a mixture of 90% inorganic and organic pigments and fillers and 10% organic oily and waxy constituents, suitably processed to have the appearance and average particle size and distribution of street soils.

1. Staple fiber soiling procedure. In the design of a procedure for soiling staple fiber, it was recognized that the important factors in carpet soiling are (1) transfer of soil to the fiber and (2) the attachment of the soil to the fiber by impact, pressure, and rubbing. It is difficult to design a machine to soil fiber by impact pressure and rubbing, and therefore tests were made to soil fiber simply by pressure application. The following test was found to give results which correlated well with service soiling tests of carpets.

a. One gram of dry finish extracted carded fiber is placed in a pint glass Mason jar with 0.5 g. of standard soil. The jar is sealed and shaken by means of an impact machine. The impact machine is a reciprocating spring arm which supports the Mason jar and swings it through a 12-in. arc, the jar colliding with two rubber-covered stops. The impact produced by the stops produced a uniform distribution of the soil on the fiber. The machine is run for 2 min., equivalent to 350 impacts.

b. The fiber with the soil distributed on the surface is passed through a roller mill having three 2-in. rolls of 4 in. width, 2 rubber-covered rolls (Rockwell hardness; R-5.0) with an intermediate steel roll (Rockwell hardness; D-33.0). The rolls have a static load of 146 lb. maintained by weights and lever arms and revolve at 20 r.p.m. The passage of the

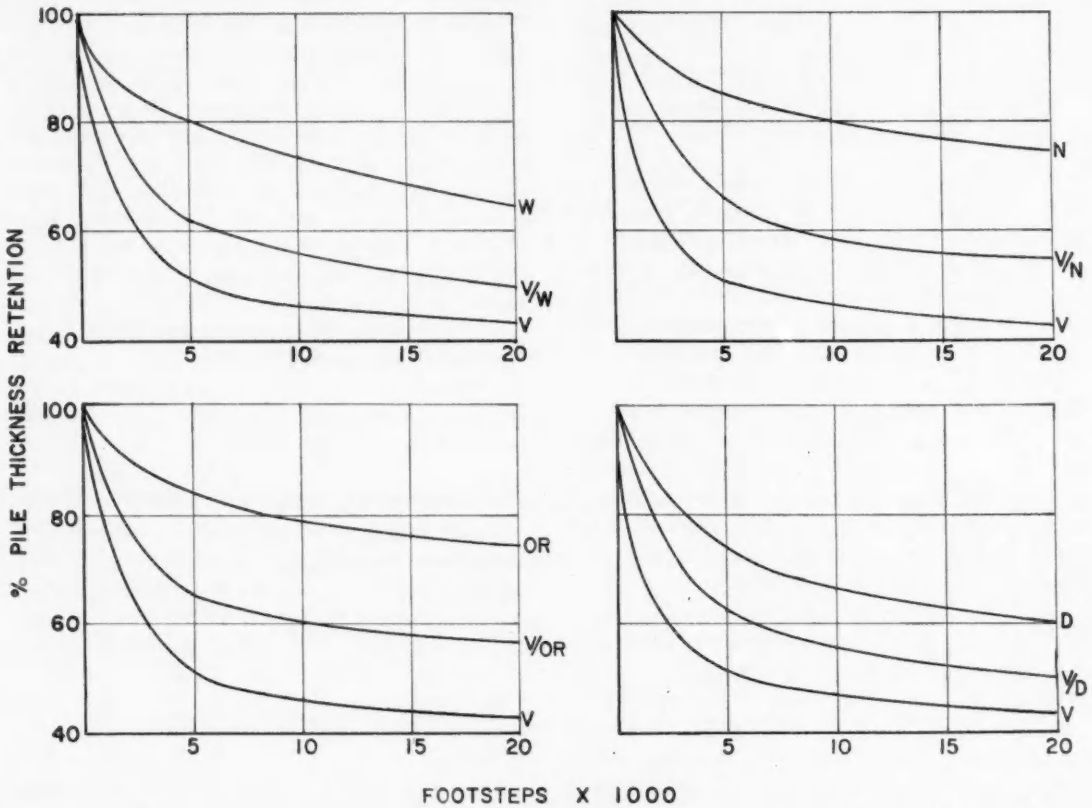

Fig. 5. Comparison of thickness-retention characteristics of blends of synthetic fibers and wool with viscose.

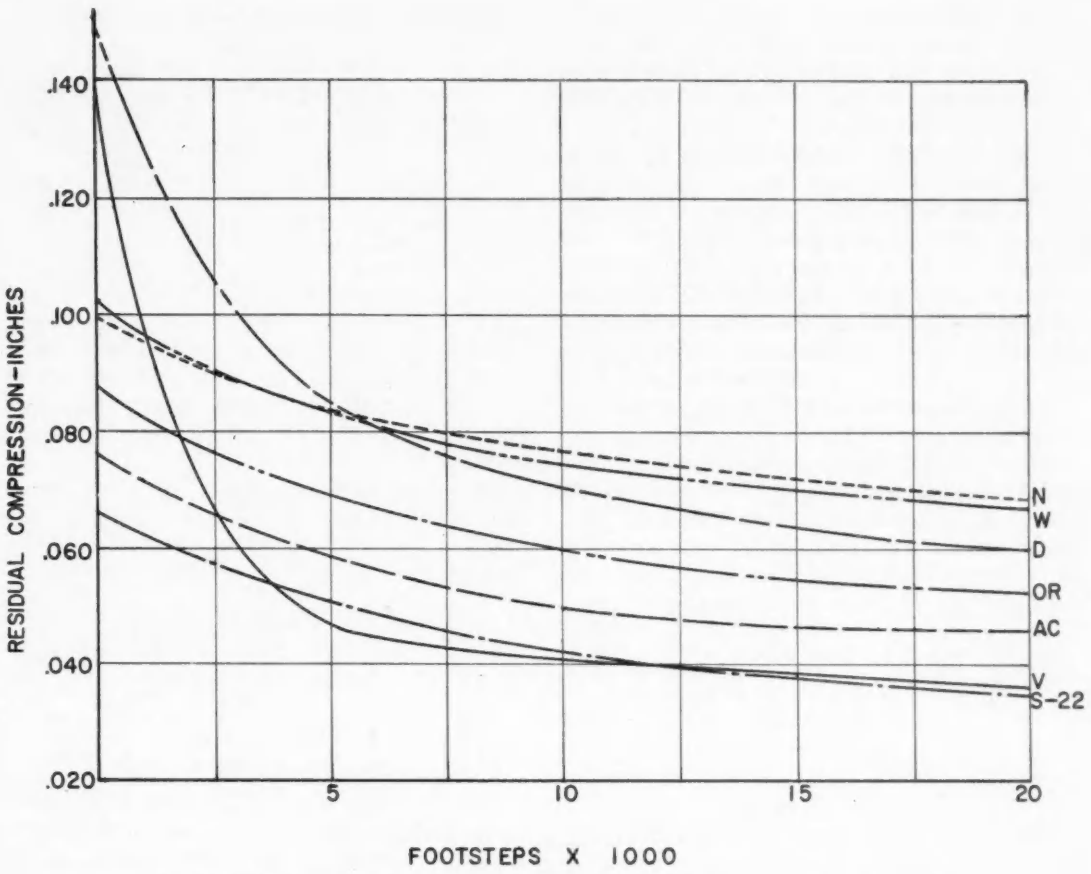

Fig. 6. Residual compression characteristics of synthetic fiber, viscose, acetate, and wool.

fibers through the lower nip and the upper nip successively is considered as one pass, and 15 passes comprise one soiling cycle.

c. The fiber is opened over a screen and vacuum line to eliminate unattached soil. This step is followed by spreading the fiber in a thin layer on a screen and blowing the fiber with a stream of dry, clean air issuing from a $\frac{3}{32}$-in. orifice at 45 lb./in.^{2}

d. The fiber is hand-formed into a pad which is placed on a glass over the aperture of a Photovolt Reflectometer, Model 610, search unit, and the reflectance is measured.

e. The fiber is resoiled following steps *a* through *d*, repeating until a condition of equilibrium soiling is found as measured by reflectance. Equilibrium soiling reflectance is defined as the reflectance obtained in nine soiling cycles. In the course of carrying out the soiling, the fibers may become badly matted, making removal of loose soil difficult. This condition requires a hand recarding of the fiber.

The determination of soil retention of the fibers soiled by the laboratory procedure is based on the removal of the soil by scouring techniques and measurement of the released soil by turbidometric measurements of the scour solution. Specifically, 1 g. of soiled fiber in 100 ml. of 0.5% Igepon T in a pint jar is subjected to shaking machine action for 5 min. at 60° C. The fiber is screened from the solution with a fine wire gauze, and the turbidity of the solution is measured with an Evelyn Colorimeter. A standard curve, plotting light transmission versus milligrams standard soil per 100 ml. detergent solution permits evaluation of the unknown.

The results obtained by turbidometric methods are not strictly quantitative since some soil may resist removal from the fiber and changes in soil particle

size distribution will occur; however, comparisons of fiber soiling properties by means other than optical are permitted. Corrections may be made for soil retained by the fiber by rechecking the reflectance of the scoured fibers.

Table IV presents a tabulation of the equilibrium soiling properties of fibers. Reflectance values are calculated to the apparent soil values. Apparent soil values for the staple fiber tests and the service tests are in the same approximate order, and correlation is judged to be good. The table also shows the milligrams of soil retained per gram of fiber at the equilibrium soiled condition. Correlation between soil retention and the apparent soil is lacking but is explained on the basis of differences in fiber contour and surface and the luster of the fiber.

A fiber such as acetate is capable of high soil retention without an equivalent gain in apparent soil, because soil lodges in the serrations in the fiber. Likewise, wool retains a relatively high amount of soil by retention under the scale tips of the fiber.

TABLE IV. Equilibrium Soiling Properties of Fibers

Fiber	Reflectance		Apparent soil	Mg. soil g. fiber
	Initial	ESR*		
Viscose, 15-den., dull	73.5	31.5	0.697	26.0
Acetate, 17-den., dull	77.0	26.5	0.905	64.0
Wool	55.5	27.0	0.808	39.0
Nylon, 15-den., brt.	60.8	25.5	0.964	28.4
Orlon, 6-den., brt.	75.5	25.0	1.082	53.0
Dacron, 6-den., brt.	72.5	28.5	0.847	39.5
Saran, 22-den., dull	52.5	19.5	1.455	26.5
Dynel, 24-den., brt.	56.0	16.5	1.926	42.0

* Equilibrium soiled reflectance.

Nylon has a relatively low soil pickup with a moderately high apparent soil. This anomaly results from nylon's relatively smooth surface which does not permit hiding of soil and the reflective characteristic of the bright fiber.

Because of increased surface area, low denier fibers such as Orlon and Dacron retain more soil than the higher denier fibers of similar surface characteristics.

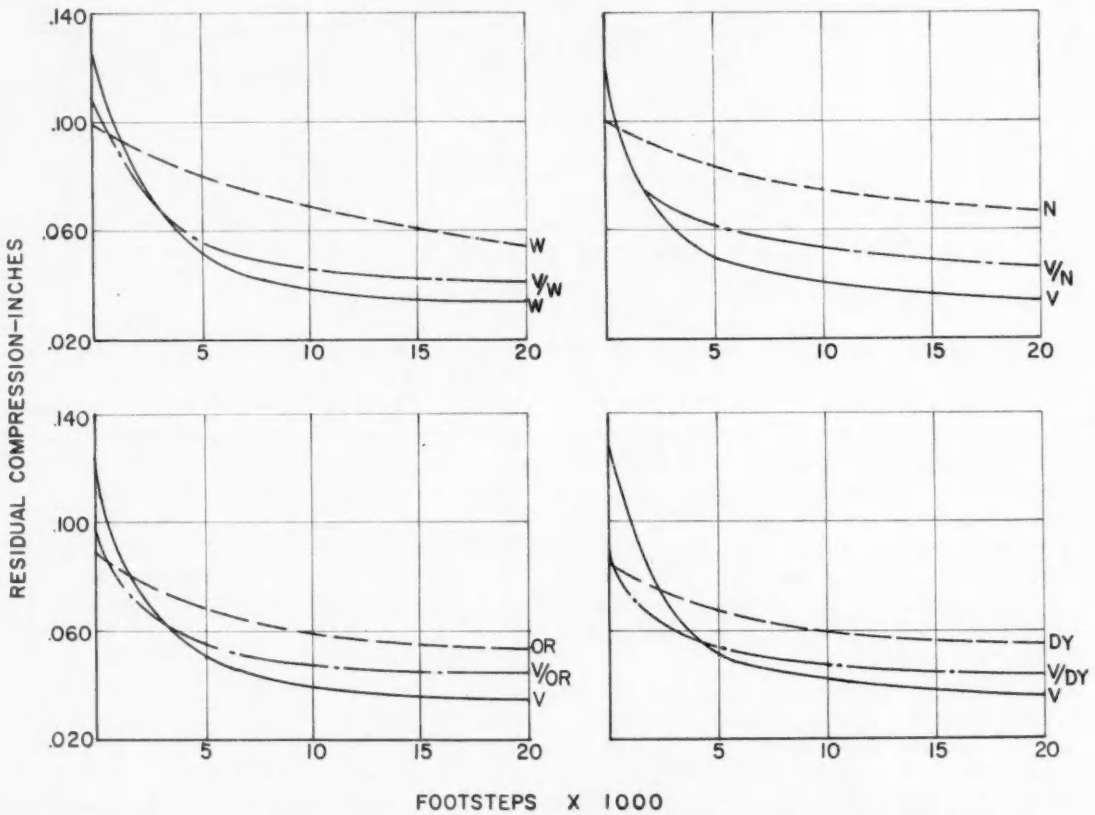

Fig. 7. Comparison of residual compression characteristics of blends of synthetic fibers and wool with viscose.

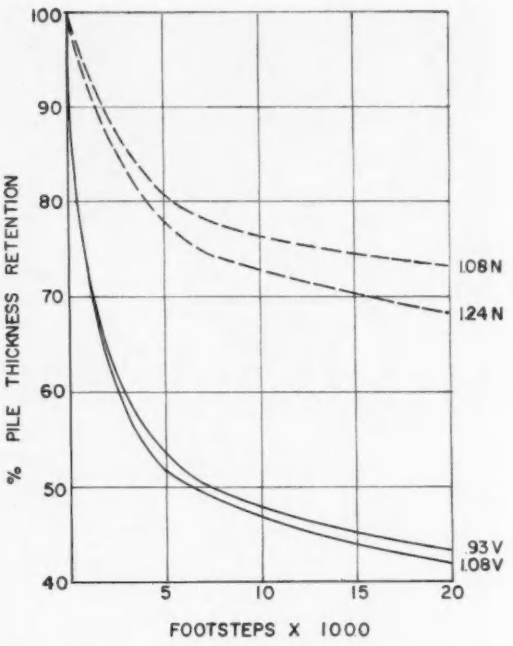

Fig. 8. Relationship of yarn size to crush recovery of nylon and viscose carpets.

B. Microscopic Examination of Carpet Fibers

The importance of the physical surface characteristics of fibers with respect to soil affinity has been shown by several investigators. Although roundness of cross section is agreed upon as a desirable characteristic for soil resistance, micro smoothness of the fiber surface is necessary if fibers are to have soil resistance.

The carpet fibers under investigation were examined microscopically by three techniques.

1. Soiled fibers were removed from service-tested carpets and cross-sectioned to determine location of soil.

2. Surface replicas of soiled fibers were examined with the electron microscope [7].

3. "Clean" carpet fibers, or fibers subjected to solvent extraction, were examined by the palladium-shadowed replicate method.

Figures 9 to 13 are cross sections of soiled viscose, acetate, wool, nylon, and Dynel. The sections of viscose, wool, and nylon show the least soil pickup which correlates with smooth round cross sections. Acetate and Dynel have surface irregularities into which soil is occluded.

Figures 14 to 18 are soiled fiber replicas of viscose, acetate, wool, nylon, and Dynel. Viscose exhibits the least soil pickup and only slight soil aggregation. Soil is packed into the serrations of the acetate fiber, whereas the remainder of the fiber is relatively free of soil. The wool fiber replica is not considered to be representative of the blend, since soil loading appears to be unusually high. Nylon and Dynel show soiling through aggregation of particles on the surface.

Figures 19 to 23 are photomicrographs of clean fibers replicated and shadowed with palladium. The replicas show the irregularities and indentations in the fiber surfaces which serve to hold soil. The nylon fiber has a fair degree of smoothness, but evidence of finish material in bands on the fiber possibly accounts for soil bonding. Finish present on these fibers is representative of that on carpets after finishing by procedures yielding "contaminant free" pile yarn.

C. Physical Measurements Related to Crush-Resistant Properties

An attempt to find correlation of the crush-recovery performance of the various carpet fibers to the following fiber properties was made.

1. Elastic-recovery properties of single filaments under repeated tensional stress.

2. Moisture regain.

The elastic-recovery properties were measured by subjecting a single filament to a load of 0.5 g./den. at an elongation rate of 10%/min., unloading at the same rate, and repeating the cycle 10 times. Elastic performance coefficients correlate roughly to service test crush-recovery data, viscose having the lowest coefficient, acetate being slightly higher than viscose, and wool being highest. The synthetic fibers are rated close to wool in the E.P.C. value. Since nylon is ranked first in crush recovery by service testing, it is concluded that the elastic-recovery measurements do not parallel service testing with respect to load, rate of load, or number of cycles.

Moisture regain is another property of the fiber which in some cases affects the crush-recovery performance. Correlation of moisture regain with crush recovery cannot be anticipated since many other factors complicate the relationships of these properties. Carpet wool and viscose have the highest regains, 13.1 and 11.75%, respectively, and demonstrate entirely different crush-recovery behavior. Acetate at

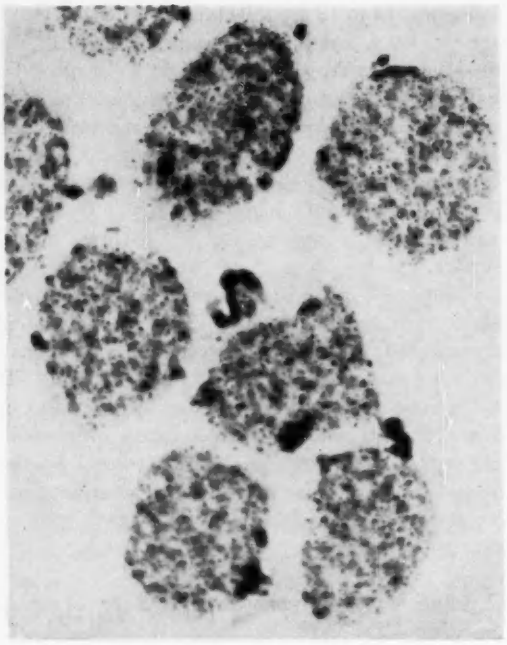

Fig. 9. Cross sections of soiled viscose.

Fig. 11. Cross sections of soiled wool.

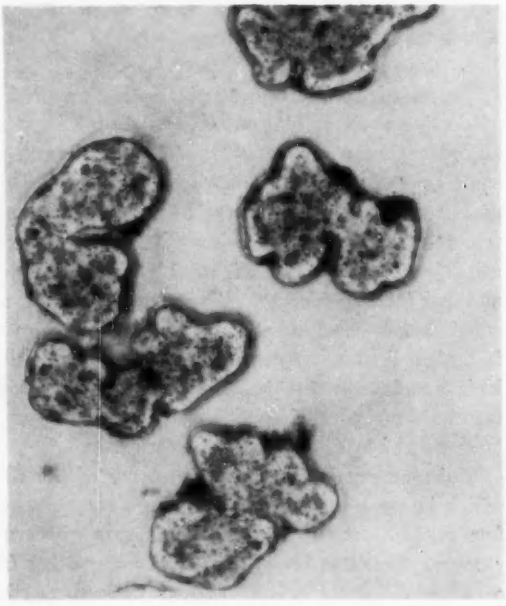

Fig. 10. Cross sections of soiled acetate.

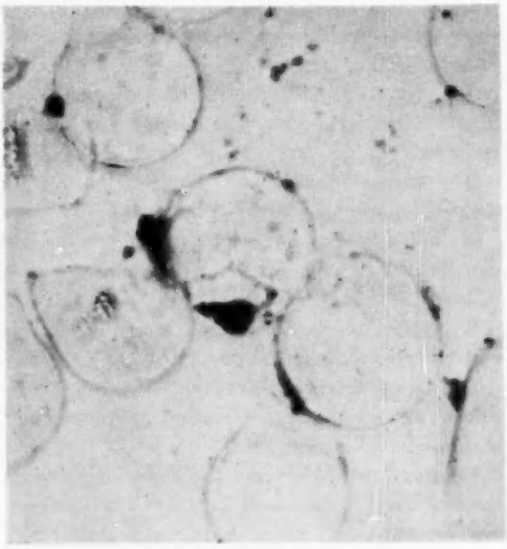

Fig. 12. Cross sections of soiled nylon.

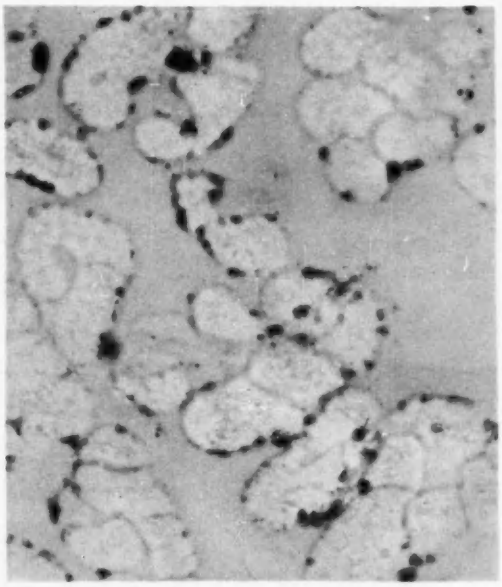

Fig. 13. Cross sections of soiled Dynel.

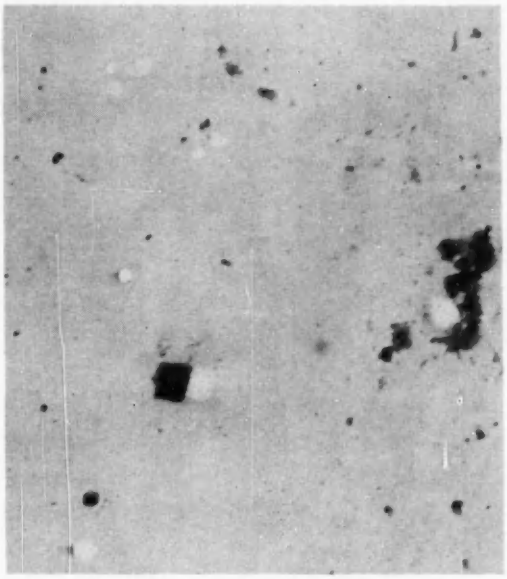

Fig. 14. Replica of soiled viscose.

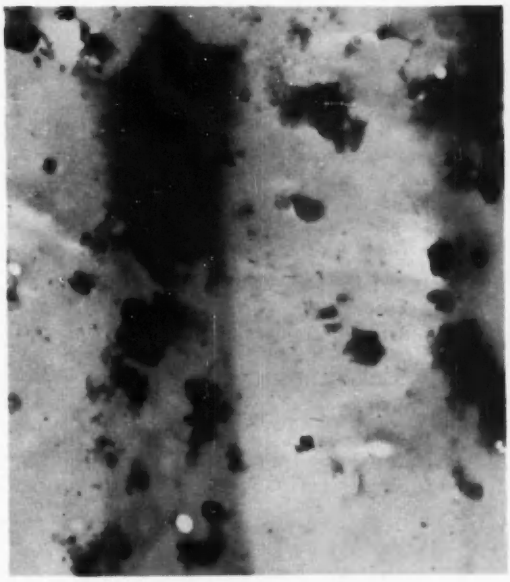

Fig. 15. Replica of soiled acetate.

Fig. 16. Replica of soiled wool.

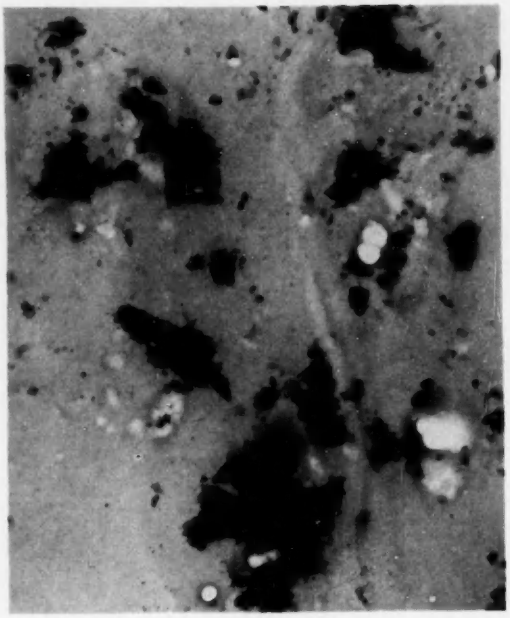

Fig. 17. Replica of soiled nylon.

Fig. 19. Unsoiled viscose. Palladium-shadowed replica.

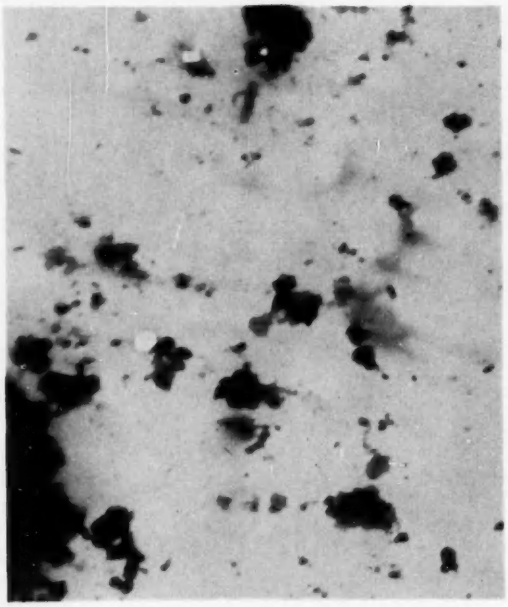

Fig. 18. Replica of soiled Dynel.

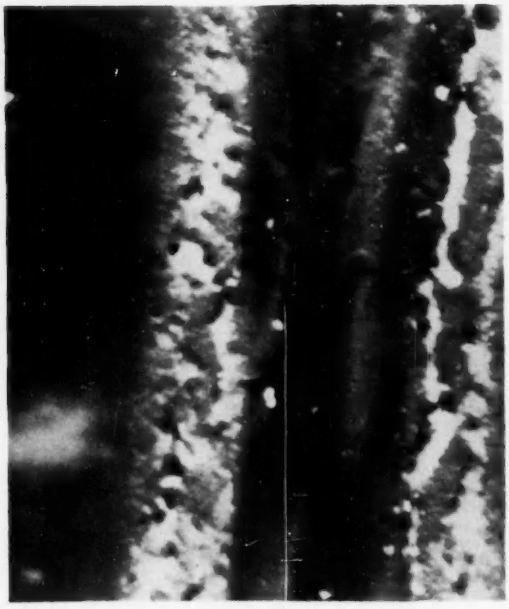

Fig. 20. Unsoiled acetate. Palladium-shadowed replica.

Fig. 21. Unsoiled wool. Palladium-shadowed replica.

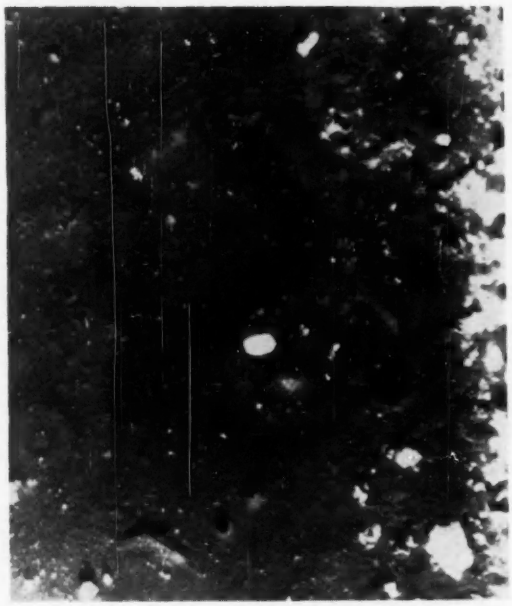

Fig. 22. Unsoiled nylon. Palladium-shadowed replica.

Fig. 23. Unsoiled Dynel. Palladium-shadowed replica.

5.51% and nylon at 3.94% are in line with improved performance at lower regain. On the other hand, Saran with a regain of 0.10% has less recovery than nylon.

Experimental work has shown viscose in carpets to have excellent crush recovery when the moisture content is very low. This finding is in agreement with the theoretical concept of the hydroplastic nature of cellulose. In the dry state hydrogen bonds between cellulose chains retard deformation of the cellulose structure. As moisture is sorbed, hydrogen bonds are broken and replaced by water bonds and swelling occurs. The cellulose structure becomes less stable to stress, and bonds are broken and re-established in the deformed state, thereby stabilizing the deformation. Wool sorbs water to a greater extent than cellulose but exhibits good crush recovery. Cystene linkages in the wool molecule are insensitive to water and are not ruptured by low stress and deformation. Sorbed water in the wool molecule actually serves to assist in recovery since it renders the molecule more mobile.

V. Summary and Conclusions

The study of various synthetic fibers, viscose, acetate, wool, and blends through service tests and in-

vestigation of fiber surface characteristics, soil pickup, luster, and electrostatic properties gives an understanding of the fiber soiling characteristics.

Basic fiber requisites for soil resistance are shown to be

1. Smoothness of surface in the macro and micro dimension.
2. High reflectivity as found in delustered fibers.
3. Absence of oily or waxy finishes or contaminants which bond soil.

The soiling property of a particular fiber is not altered by the presence of another fiber in the blend so that the blend will soil at a level proportionate to the properties and ratio of the fibers making up the blend.

Since the soiling behaviors of synthetic/viscose blends are directly related to the soiling properties of the component fibers and since the electrostatic properties of the blends are not directly related to the electrostatic properties of the component fibers, no relationship of static charge to soiling properties can be proved for individual fibers.

The study of crush recovery of the various fibers proves the synthetics, such as nylon and Orlon, to outperform wool in retention of original pile height and maintenance of residual compression. Other synthetics such as Dynel, Dacron, and Saran are equivalent or nearly equivalent to wool in crush resistance. Crush resistance of the synthetics is partially attributed to their nonhydroplastic properties. 50/50 blends of viscose and synthetics or wool do not exhibit crush-resistant properties equivalent to the average of the crush properties of the respective fibers entering the blend. No explanation for the inferior behavior of the blends is suggested.

Pile density is not considered an important factor controlling crush recovery when fibers of different specific gravity are compared, and the pile density varies proportional to the specific gravity. When corrections for pile densities are made by increasing yarn weights, slight shifts are observed in crush recovery favoring the higher pile density. These shifts are insufficient to change the ranking of the fibers for crush recovery.

Poor crush-recovery characteristics of viscose fibers are attributed to the high moisture regain and hydroplasticity property.

Acknowledgments

The work described above is the result of the combined efforts of the Firth Carpet Company and the Research and Development and Textile Research Departments of American Viscose Corporation. The author is grateful for the guidance and assistance as well as the preparation of samples by R. Matthews and B. Schneeweis of the Fifth Carpet Company. The preparation and interpretation of Photomicrographs are the work of F. F. Morehead of the R.D.D. of A.V.C. The author further recognizes the valuable assistance of K. L. Whitney of the T.R.D. of A.V.C. in programming the work.

Literature Cited

1. Bacon, O. C., and Smith, J. E., "Detergent . tion," *Ind. Eng. Chem.* **40**, 2361–2370 (1948).
2. Compton, J., and Hart, W. V., "A New Approach to the Study of the Soiling and Soil Retention Properties of Textile Fibers," TEXTILE RESEARCH JOURNAL **23**, 158–168, 418–423 (1953).
3. Fortess, F., and Kip, C. E., "Factors Influencing the Soiling of Acetate Carpets," *American Dyestuff Reporter* **42**, 349–359 (1953).
4. Kubelka, P., and Muck, F., *Z. Tech. Physik* **12**, 593 (1931).
5. Leonard, E. A., and Schwartz, E. W. K., "Measurement of Fabric Soiling," *American Dyestuff Reporter* **41**, 332 (1952).
6. Masland, C. H., II, "Soil Retention of Various Fibers," *Rayon Textile Monthly* **20**, 573–574, 654–656 (1939).
7. Morehead, F. F., "The High Contrast (Wide Field) Electron Microscope Objective and Fiber Replicas," TEXTILE RESEARCH JOURNAL **22**, 379–384 (1952).
8. Private communication, Bigelow Sanford Carpet Company.
9. Reich, I., Snell, F. D., and Osysow, L., "Reflectance as a Measure of the Soil Content of Cotton Fabric," *Ind. Eng. Chem.* **45**, 137–141 (1953).
10. Sanders, H. R., and Lambert, J. J., "An Approach to a More Realistic Cotton Detergency Test," *J. Am. Oil Chemists' Soc.* **27**, 153–159 (1950).
11. Sayre, J. F., and Weldon, A. J., "A Study in Three Fiber Blends," *Modern Textiles* **35**, 32, 33, 41–44, 52–53, 68 (1954).
12. Schappel, J. W., "Tufton—Rayon's Newest Carpet Fiber," *Modern Textiles* **34**, 31, 87–88 (1953).
13. Snell, F. D., Snell, C., and Reich, I., "The Nature of Soil to be Deterged and Its Bonding to the Surface," *J. Am. Oil Chemists' Soc.* **27**, 62–68 (1950).
14. Weatherburn, A. S., and Bayley, C. H., "The Soiling Characteristics of Textile Fibers," Part I, TEXTILE RESEARCH JOURNAL **26**, 549–558 (1955).
15. Whitney, K. L., and Schappel, J. W., "Carpet Soiling," *American Dyestuff Reporter* **43**, 143–147 (1954).

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Letter to the Editor

Short communications in the form of Letters to the Editor are intended to provide prompt publication of significant new research results and to permit an exchange of views on papers previously published in the JOURNAL. These communications are not submitted to formal review as are research papers, and the editors do not assume any share of the author's responsibility for the information given or the opinions expressed. When work previously published in the JOURNAL is the subject of critical comment, the authors of the original paper are given an opportunity to submit a reply, which will be published concurrently when possible.

Identification of Textile Fibers by Dye Staining Techniques

State of Maryland
Department of Health
Baltimore, Maryland
November 22, 1955

To the Editor
TEXTILE RESEARCH JOURNAL

Dear Sir:

For the past thirty years, the Division of Bedding and Upholstery of the State of Maryland Department of Health, has been charged with the enforcement of the law requiring the truthful labeling of pillows, mattresses, comforts, cushions, and upholstered furniture.

We have recently noticed in our work the increasing use of some of the new man-made synthetic fibers as filling material, especially as a replacement for feathers and down in pillows and comforts. Consequently, this Division has found it necessary to devote its attention to the problem of finding methods for the rapid and accurate identification of these newer fibers together with the older fibers which may be used as adulterants.

Since dye staining techniques were thought to be the most fruitful line for investigation, we directed our study to an examination of a selection of various identification stains on the market.

It is with the thought that readers of TEXTILE RESEARCH JOURNAL will be interested in the technique which we have established that we present the following brief summary of our experimental results and outline of the procedure that has been adopted.

We investigated the staining behavior of twelve fibers: acetate, viscose, Bemberg, cotton, these being cellulose-base fibers; wool, Vicara, and nylon, which are protein and polyamide fibers; and the following polyester and polyacrylic fibers, namely, Dynel, Acrilan, Orlon 81,[1] Orlon 42,[1] and Dacron.[2]

Although the various stains are quite useful in distinguishing the subject fibers, we find that Du Pont Identification Stain No. 4 seems to be over-all the most effective. It gives more vivid and contrasting colors on a greater number of fibers than any of the other stains, consequently requiring fewer secondary tests for the final identification of a sample.

When the authors took a mixture of all 12 fibers and stained them with Du Pont No. 4, each fiber was easily distinguished and picked out (except Orlon 42 and Dacron) upon color comparison with known samples. Even a doubtful separation could be made between Orlon 42 and Dacron if both were present for purposes of comparison.

We have therefore adopted it as the basis of our recommended scheme of identification of the 12 subject fibers.

All the cellulosic fibers and Acrilan, Orlon 81 filament, and Dynel can be easily picked out from an all-fiber sample. Wool, Vicara, and nylon show various shades of purple-brown which with a little experience and careful comparison with known standards can be distinguished easily. Dacron and Orlon 42 give almost indistinguishable shades of yellowish orange and consequently may have to be distinguished by boiling in 5% H_2SO_4 solution for upwards of 30 min. This treatment causes the Orlon 42 to become pink, while the Dacron assumes a golden yellow. A confirmatory test is given when, upon just covering the stained fiber with cold con-

[1] Du Pont acrylic fiber.
[2] Du Pont polyester fiber.

centrated hydrochloric acid, the Dacron immediately turns deep red, while the Orlon 42 remains unchanged or turns somewhat orange.

If a separation is required between wool, Vicara, and nylon, this can be accomplished by boiling the purple-brown stained sample in an aqueous solution of 4% sodium carbonate containing 1% Texstrip for 5 min. This treatment causes the wool to become white, the Vicara yellow, and the nylon pink. If the Texstrip is added pinchwise to the boiling 4% sodium carbonate solution containing the wool-Vicara-nylon mixture, these color changes show up with dramatic suddenness.

Recommended Procedure

1. Immerse the unknown sample of fibers in a freshly prepared boiling 1.0% aqueous solution of Du Pont Identification Stain No. 4, using a 20:1 bath to fiber ratio.

2. Run bath at the boil for 1 min., remove sample, rinse in cold water, and dry.

3. Carefully compare the color of the stained sample with known fibers already dyed in Du Pont No. 4.

4. Should the unknown prove to be a fiber mixture, it is recommended that the various fibers be picked out in the following order:

Reddish orange (acetate)
Shades of blue and green (cotton, Bemberg, rayon)
Shades of purple-brown (wool, Vicara, nylon)
Reddish brown (Acrilan)
Brown (Dynel)
Gray-blue (Orlon 81)
Shades of yellow-orange (Dacron and Orlon 42)

5. Should there be any difficulty in identifying wool, Vicara, or nylon, immerse the stained fibers (purple-brown) in boiling 4% sodium carbonate solution containing 1% Texstrip for about 5 min. Vicara becomes yellow, nylon turns pink, while wool is decolorized and partly dissolved.

6. Should there be any difficulty in distinguishing Dacron from Orlon 42, boil the material in 5.0% sulfuric acid for 5 min. Orlon 42 becomes pink, while Dacron yields a gold shade (or remains unchanged). A more rapid method is to drop the sample in a small amount of concentrated hydrochloric acid, in which case the Dacron turns crimson while the Orlon 42 remains unchanged . Also Orlon is soluble in concentrated nitric acid or boiling dimethylformamide, while Dacron is not.

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INDUSTRIAL SECTION

Finishing of Synthetic Fabrics

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Introduction

Finishing of the fabric is one of the most important of the fabric variables. It provides a means of modifying the fabric properties without changing the fibers' composition. Thus, a fiber can be standardized for its best all-round properties and the finishing relied upon to change the fabric properties for the particular end use desired. Furthermore, it is often the only way in which many of these properties can be obtained.

This paper deals with the finishing of synthetic fabrics. However, it also includes information on the finishing of fabrics containing the natural fibers, because (1) with a knowledge of the properties that can be imparted to natural fibers, the advantages that can be gained by the finishing of synthetics can be better appreciated, and (2) blends of natural with synthetic fibers are becoming more and more important. Although general finishing practices are discussed, most of the paper is concerned with the new durable, functional finishes which either have already become commercially important or appear to have commercial possibilities. Coating of fabrics is not discussed.

Fabric finishing, as the name implies, is the last processing to which the fabric is subjected. It is designed to impart a specific property or properties to the fabric. The fabric may be mechanically finished such as by being heat set or Sanforized,[1] or the finishing may involve the addition of chemicals such as water repellents or resins.

The finishing materials are usually applied to the fabric from an aqueous solution, dispersion, or emulsion by immersing the fabric and then passing it through squeeze rolls to remove the excess liquor. The fabric is then dried and cured at a higher temperature if the finishing material requires curing.

At this time, let us enumerate some of the more important properties that can be imparted to the older fibers by finishing. For cellulosic, wool, and acetate fabrics, these properties are listed below.

Improved Fabric Properties

1. Wrinkle resistance
2. Water repellency
3. Spot resistance
4. Soil resistance
5. Fire resistance
6. Change in hand
7. Shrinkage control
8. Increased wear life
9. Increased wash fastness of dyes
10. Durable mechanical finishes

Wrinkle Resistance

One of the most important fabric properties for wearing apparel is resistance to wrinkling. Most of the synthetic, hydrophobic fibers inherently are more resistant to wrinkling than the natural fibers such as cotton, wool, and rayon, especially under conditions of high humidity. The ability of a fabric to recover from wrinkling is determined primarily by its elastic recovery from deformation. This elastic recovery may be immediate and complete, in which case the wrinkles will vanish immediately; or it may be delayed, in which case it will take time for the wrinkles to disappear.

The use of thermosetting resins of the urea-formaldehyde, melamine-formaldehyde and ethylene-urea-formaldehyde types on cellulosic fabrics has resulted in a great improvement in their recovery from wrinkling. Although these products are called

[1] Sanforize: Trademark of Cluett, Peabody & Co.

thermosetting resins, they are mostly in monomeric form when applied to textiles in wrinkle-resistant finishes. The molecules are therefore sufficiently small to diffuse into the cellulosic fiber where they cross link between adjacent cellulosic chains. Since these molecules are capable of reacting with themselves, some polymerization probably occurs. It is believed that their chemical reaction with the cellulose to cross-link adjacent chains is primarily responsible, however, for the improvement in the elastic recovery of the fiber. Figure 1 schematically shows a melamine-formaldehyde molecule cross-linking two adjacent cellulosic chains.

Figure 2 shows stress-strain curves of an untreated and of melamine- and urea-formaldehyde-treated rayon fibers taken from a rayon fabric. The increase in the slope of the straight-line portion of the stress-strain curve shows that the elastic recovery of the rayon fiber has been increased by the resin treatment. Thus, it can be seen that resin finishing of a rayon fabric has resulted in a fundamental change in the rayon fibers.

Stress-strain curves of fibers, yarns, and fabric, both untreated and treated with urea formaldehyde (UF), are shown in Figure 3. It is interesting to note that the elasticities of the fiber, yarn, and fabric are all increased by the resin treatment. Therefore, it appears that the increase in elasticity of the fabric is obtained by an increase of the elasticity of the fibers which is carried through to the yarns and finally to the fabric [2].

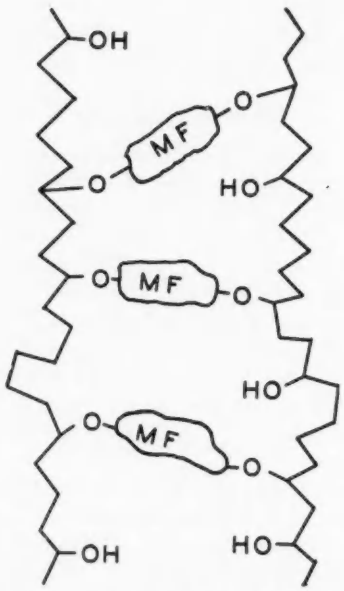

Fig. 1. *MF* reaction with cellulose.

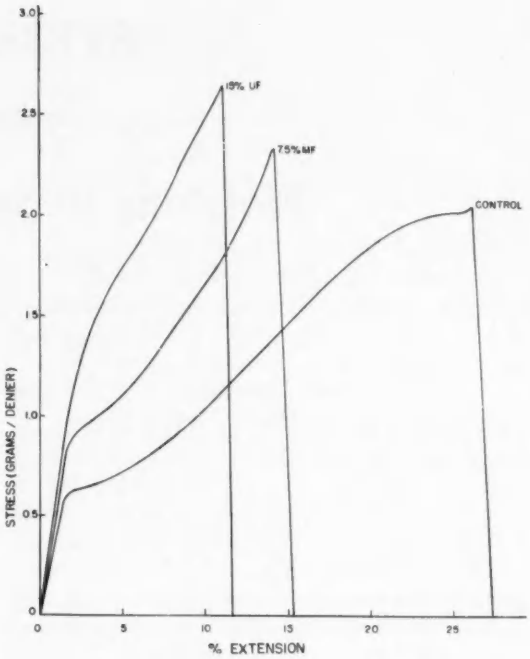

Fig. 2. Stress-strain curves for rayon fibers.

Rayon fabrics and fabrics composed of rayon blended primarily with acetate, but also with nylon and Dacron,[2] are treated with thermosetting resins to produce a wrinkle-resistant finish with shrinkage control and improved color retention during washing. This type of fabric has been used in large quantities in outerwear fabrics. The addition of a water repellent, such as Permel [3] Resin (a melamine-resin based durable water repellent) or a silicone, provides water repellency and resistance to water-borne stains as well as increased resiliency. Also, improvements in abrasion resistance and strength are obtained over that of the rayon treated with resin alone. The Permel Resin also produces a wool-like hand on all rayon or on blends of rayon with the synthetic, hydrophobic fibers. Starting in 1950 when wool became scarce and high-priced, large quantities of rayon and blends of rayon with acetate were treated with a thermosetting resin plus a water

[2] Regular Trademark of E. I. du Pont de Nemours & Co., Inc.

[3] Trademark of American Cyanamid Company.

repellent, chiefly Permel Resin, to produce a wrinkle-resistant fabric with a wool-like hand. Fabrics of this type have been in large-scale use since that time.

Wash and Wear

One of the most important developments in wearing apparel in recent years has been wash and wear fabrics. For the purposes of this paper wash and wear fabrics are defined as those which, after washing and drying, appear relatively free of wrinkles and can be worn with little or no ironing.

Historically, the first wash and wear fabrics were made of the synthetic, hydrophobic fibers. Lately, the trend in the use of synthetic fibers for wash and wear fabrics has been toward a blend of fibers such as Dacron and Orlon [4] with cotton, rayon, and wool. One of the popular blends of this type is the 65% Dacron and 35% cotton fabric. Actually, the wrinkle-resistant cotton and rayon fabrics which have been on the market for a number of years have wash and wear properties to some degree. However, it was not until early in 1955 that cotton finishers, producing more highly wrinkle-resistant cotton fabrics, promoted them as wash and wear fabrics.

The important factors in producing a wash and wear finish are (1) construction of the fabric, (2) color pattern of the fabric, and (3) the finish. The

[4] Regular Trademark of E. I. du Pont de Nemours & Co., Inc.

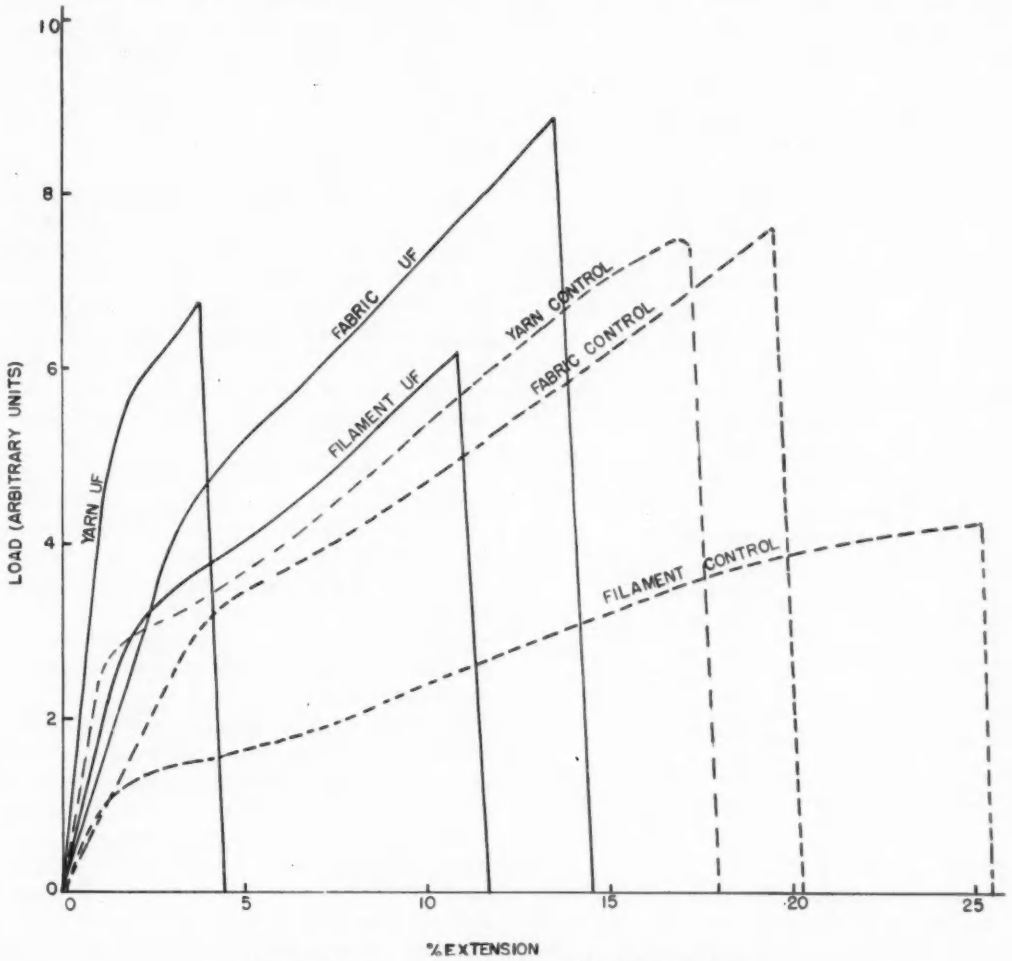

Fig. 3. Load-extension curves, treated and untreated rayon.

fabric should be constructed to allow the greatest freedom of movement of the fibers and yarns in the fabric. With such a construction, the fabric more easily recovers from the forces to which it is subjected during the washing and drying operation.

The texture of a fabric is important in camouflaging or hiding wrinkles. Napped or pile fabrics show less wrinkling after washing than a smooth-surfaced fabric. A textured fabric such as an embossed or a puckered fabric appears less wrinkled than a smooth fabric. A solid-colored fabric shows more wrinkles than a many-colored pattern.

Thermosetting resins are used in wash and wear formulations for cotton fabrics to provide wrinkle resistance, greater resiliency, shrinkage control, decreased water absorption, decreased time of drying and less wrinkling after washing and drying. Melamine and ethylene-urea formaldehyde resins are chiefly used for this type of finish primarily because their durability to washing is greater than that of urea formaldehyde.

In a study of some of the factors involved in wash and wear finishes, typical wash and wear formulations based on melamine-formaldehyde resins were applied to 80 × 80 cotton fabric and wrinkle-recovery measurements were made on the fabric during drying. The wrinkle-recovery measurements were made by creasing the fabric and then measuring the angle of recovery after a 5-min. period. Figure 4 presents a plot of wrinkle recovery versus time of drying of these fabrics after one washing followed by spinning in a home-type automatic washing machine. As can be seen, the wrinkle recovery of the untreated fabric decreases during drying to a minimum just before the fabric is dried. On the other hand, the wrinkle recovery of the treated fabrics remains fairly constant throughout the drying operation, increasing slowly with time of drying. It would appear from the above data that the reason that the untreated fabric is wrinkled is primarily because of poor recovery during drying from the wrinkling that occurred during the washing. On the other hand, it would appear that the treated fabrics have wash and wear properties because of their ability to recover from wrinkling during all stages of the drying operation.

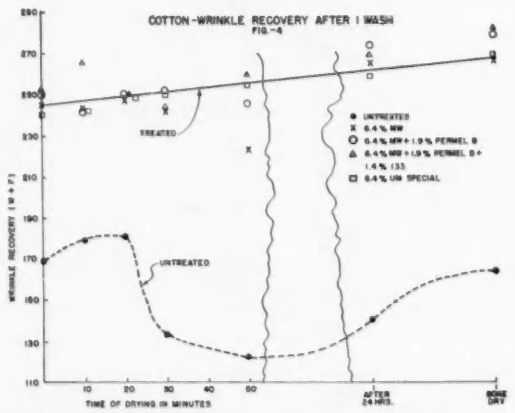

Fig. 4. Cotton-wrinkle recovery after one wash. MW and UM Special are MF resins. 133 is a thermoplastic.

Rayon

Considerable development work is being conducted on wash and wear finishes for rayon. It appears that more thermosetting resin is required with rayon than with cotton to obtain satisfactory wash and wear properties.

Blends

At the present time, most of the blends of the synthetic, hydrophobic fibers with cotton, rayon, and wool are being sold as wash and wear fabrics without benefit of resin treatment. However, development work is being conducted on resin finishes to improve the wash and wear properties of the blended fabrics. The same type of resin formulations used on cotton appears to be suitable for these blends with less resin being required than with cotton alone.

Resin Treatment of Nylon

The first important application of resins to nylon was made during World War II. Melamine formaldehyde was used on nylon insect netting to produce stiffness, to reduce yarn slippage, and to bind pigments used for coloration.

Since that time, the use of resins on nylon has become widespread. Textile resins have been used extensively in altering the hand of different types of nylon fabrics. For example, nylon marquisettes which are used primarily for curtains have a limp, dead hand. In order to make this type of fabric more salable, it is desirable to impart a crisp finish. There are two classes of resins suitable for this purpose. Thermoplastic resins such as the acrylates produce stiffness, but the finish has limited durability and does not have the desired crispness. Melamine-formaldehyde resin produces a crisp finish with varying degrees of stiffness depending on the amount of

resin used. This finish is smooth and resilient as well. The durability of melamine resin finishes on nylon to handling, washing, and dry cleaning is excellent. This resin finish also reduces yarn slippage.

Melamine-formaldehyde resins are widely used for finishing nylon taffeta to produce varying degrees of stiffness from very slight to the full stiffness of the bouffant, parchmentlike finish used in petticoats. Partially polymerized urea-formaldehyde resins also may be used to impart stiffness to taffeta, but the same degree of resiliency, smoothness, and durability cannot be obtained; also, urea-formaldehyde-treated nylon fabric has a tendency to release formaldehyde gas on storage, especially under conditions of high humidity and temperature.

Heavy-weight nylon mesh fabric is resin-finished to make it suitable for use in shoes. The best finishes on nylon shoe mesh are obtained by a combination of a melamine-formaldehyde resin and Permel Resin. This combination of resins produces a stiff fabric that remains firm and resilient through the constant flexing to which a shoe fabric is subjected and provides resistance to spotting by water-based materials.

Unfinished, puckered nylon is usually a lightweight, sheer fabric with a dead hand. It is common practice to add a small amount of a melamine-formaldehyde resin to this type of fabric to impart a crisp, resilient hand.

Nylon lace is another fabric which is enhanced by a resin finish. The application of moderate amounts of melamine resin will impart stabilization, durable crispness, and prevent curling of the edges.

Lightweight, sheer nylon fabrics are also commonly treated with melamine formaldehyde to provide body and resiliency to the fabric.

A few years ago, Raschel nettings were made chiefly of cotton. Then, it was found that finer, lighter weight Raschel nettings could be made of nylon because of its greater strength, but the untreated fabric had little practical use. However, Raschel netting treated with a high solids application of melamine-formaldehyde resin has been used extensively for women's dresses and petticoats. Treated with melamine-formaldehyde resin, the nylon Raschel net has a finish with a very stiff, resilient, smooth hand that is durable to both washing and dry cleaning. The melamine-formaldehyde resin finish has one important drawback, however; it increases the flammability of nylon. With the enactment of the Federal Flammable Fabrics Act of 1954, a new finish had to be found. The increase in flammability of resin-treated nylon fabrics is a problem only with very lightweight fabrics such as Raschel netting. This problem exists with lightweight fabrics because (1) very high solids of resin (up to 65%) are applied to get the desired finish and (2) the ratio of air to fabric surface is high. Both of these factors are important contributors to the flammability of the fabric.

Flameproofed Nylon

Unfinished nylon fabric has limited flammability, usually melting when exposed to a flame. For example, when the flame of a burning match is held near untreated nylon Raschel netting, the fabric starts to burn and then melts. The heat of fusion that accompanies the melting lowers the temperature of the flame. Furthermore, as the nylon melts it drops away from the fabric, thereby removing some of the heat and combustible by-products. These two effects combine to lower the temperature of the flame below the ignition temperature of the nylon. It is believed that a urea or melamine resin finish raises the melting point of the treated nylon. These resins also prevent the melted nylon from readily dropping away. As a result, the resin-treated nylon may be flammable.

It has been found that the use of thiourea or thiourea-formaldehyde resin in conjunction with urea-formaldehyde resin gives a nonflammable, stiff finish to nylon fabric. It is believed that the reason thiourea formaldehyde flameproofs nylon is that it lowers its melting point.

A melamine-formaldehyde finish for nylon Raschel netting has the following advantages over a finish obtained with a blend of thiourea formaldehyde and urea formaldehyde: (1) superior hand, (2) greater durability, (3) less tendency to change color on treatment, and (4) less tendency to release formaldehyde from stored fabric. However, the finish obtained with a mixture of thiourea formaldehyde and urea formaldehyde is cheaper and makes the nylon fabric nonflammable. Therefore, it has found wide acceptance.

Nonwoven Fabrics

Considerable progress has been made in the development of new and improved nonwoven fabrics. One of the most interesting developments has been a resin-treated nonwoven fabric used for wearing

apparel composed of a mixture of nylon and rayon fibers. Some of the first fabrics of this kind were finished with natural rubber latex and had the deficiencies of discoloring and stiffening on aging and poor resistance to dry cleaning. It was found that a mixture of melamine formaldehyde and certain synthetic latices overcame these deficiencies. Most of this type of fabric is now finished in this manner by a number of manufacturers of nonwoven fabric. This mixture of resins gives a soft, resilient, wrinkle-resistant fabric which is durable to washing and dry cleaning. The fiber composition can be varied to include other fibers such as cotton, Dacron, and acetate. The fabric can be varied in thickness and density, but the most popular one weighs approximately 3 oz./yd.^{2} This fabric which has been used for interfacings and for petticoats has grown very rapidly in volume in the past year or two. A limited amount of this fabric has even been used for outerwear such as men's slacks and women's skirts.

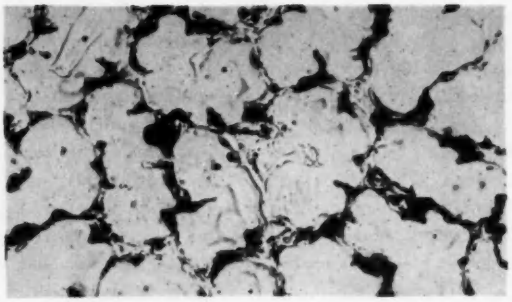

Fig. 5. Cross section of soiled acetate yarn.

Soil Resistance

Treatment for soil resistance is one of the most interesting new developments in the finishing of

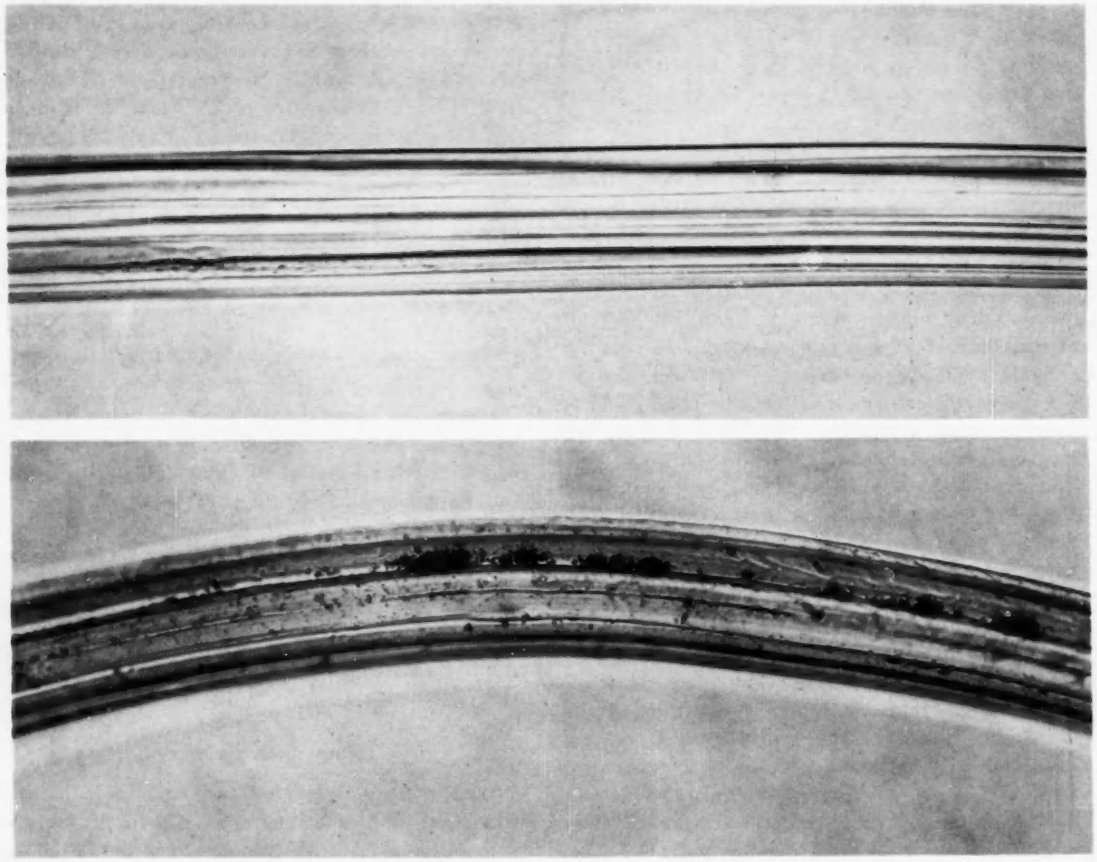

Fig. 6. Optical micrographs of serrated viscose fiber (500 ×). Top, unsoiled; bottom, soiled.

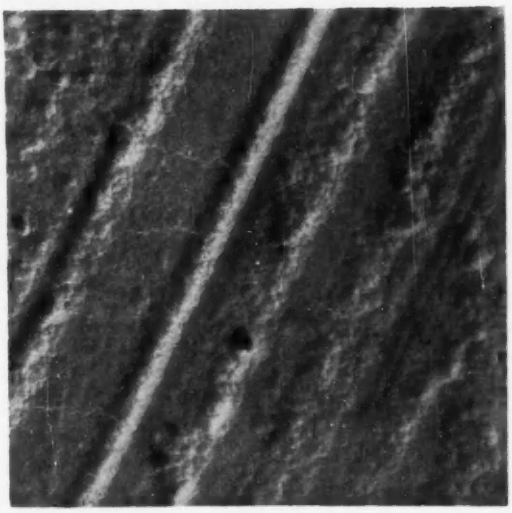

Fig. 7. Electron micrograph of the surface of serrated viscose fibers (20,000×).

fabrics. A change in the American way of living has brought about the need for a soil-resistant finish for fabrics. An increasing number of ranch houses with entrances directly into the living room, wall-to-wall carpeting, a growing preference for pastel colors in rugs, draperies, automotive fabrics, etc., and a trend toward lightening household chores have made American women aware of the need for a soil-retardant finish.

A soil-resistant finish reduces the rate of soiling of a fabric. Its main function appears to be the prevention of firm attachment of soil to the fabric. Thus, a fabric treated with a good soil-resistant finish will appear less soiled in use and is easier to clean than an untreated one.

Soil Retarding Agents

Early work on soil resistance was concerned mostly with clothing. The application of starch [12], for example, made shirts soil less rapidly by giving the fabric a smoother surface. Colloidal silica was the first of the newer developments [1], but it produced a harsh hand. The addition of softeners to the silica improved the hand but decreased its soil-resistant effect. A mixture of alumina and silica, Juvenon Soil Retardant, was the next development in the soil-retardant field [3]. It provides good soil retardancy with little effect on hand or other fabric properties. It is now being used in commercial quantities.

Factors Involved in Soil Retention

The factors involved in soil retention are shown below.

Soil particle size and shape [9]
Fiber shape [7]
Fiber surface smoothness [5]
Oil bonding [4, 5, 6, 11]
Electrostatic effects [11]

Soil Particle Size and Shape

Fibers have small irregularities in their surfaces. These irregularities can serve as sites to collect dirt. These sites increase in number as their size decreases; thus, it would be expected that smaller soil particles, particularly those measuring less than a micron, would be retained tenaciously in greater numbers than larger particles.

Fiber Shape and Smoothness

Figure 5 shows a cross section of an acetate yarn that has been soiled. It can be seen that most of the dirt has collected in the serrations of the fibers. The top portion of Figure 6 is a photomicrograph of an unsoiled rayon fiber. The lower part shows the same type of fiber after soiling and vacuum cleaning. Dirt fills the serrations and clusters around the serrations. In addition to relatively large serrations, rayon fibers have micro roughnesses, in the range of tenths of a micron as shown in Figure 7.

In Figure 8, a cotton fiber is shown to have both micro and macro rugosities. Soil concentrates in the fiber folds of cotton, as shown in Figure 9, in much the same manner as it collects in the serrations of viscose.

The surface of wool fibers is rough like that of other natural fibers. The macro roughness of wool is shown in Figure 10, which is an optical micrograph. The less widely recognized micro rugosities of the epicuticle are readily evident in the electron micrograph of a wool fiber. When wool fibers are soiled, the soil concentrates in localized rough areas, such as the scale tips, as well as in the micro rugosities as shown in Figure 11.

Not only do the cellulosic fibers and wool show these rough surfaces, but when examined with an electron microscope, the so-called smooth fibers, nylon (Figure 12), polyester fibers (Figure 13), and acrylic fibers (Figure 14) also show the same irregularities which could serve as sites for dirt to accumulate.

Oil Bonding

Soiling is intensified by fiber oiliness. This fact has been observed in our laboratory on wool and viscose fibers and by others [4] on acetate fibers. The manner in which oil exerts this effect is a combination of oil wetting of soil particles and mutual attraction of organic oil for organic fiber.

Electrostatic Effects

Electrical charge probably does not play an important role in soil retention as shown by the fact that although the rate of soiling of various fibers is markedly changed by treatment with Juvenon Soil Retardant R, this treatment has no effect on the electrostatic properties [10].

Reduction of Soiling Rate

Dirt Barrier

A soil-resistant finish appears to act like a soil barrier [3, 5]. That is, the colorless soil-retardant particles occupy sites on the fiber which would otherwise be occupied by soil particles. Once a carpet is "saturated" with soil or the soil retardant, all subsequent impinging soil finds no unoccupied sites. The dirt cannot become firmly attached. The soil-retardant particles also fill in imperfections in the fiber surface, making it relatively smooth.

Figure 15 shows a rayon fiber which has been treated with a soil-resistant finish. The serrations appear to be smoothed over by a film so that dirt cannot easily lodge therein. Figure 16 shows a treated rayon fiber that has been soiled. This photomicrograph shows that the number of soil particles is greatly diminished by the presence of the soil-retardant finish. Compare Figures 15 and 16 with Figure 6.

Electron micrographs of the surface of serrated viscose fibers were taken before and after treatment with Juvenon Soil Retardant R and after the fibers were soiled. Figure 17*a* shows that Juvenon Soil Retardant R forms a fairly continuous coating over the unserrated portions of the surface. Figure 17*b* shows that the serrations appear to be filled with Juvenon Soil Retardant R, but often the surfaces around the serrations seem relatively bare.

The electron micrograph (Figure 17*c*) shows the presence of a large number of soil particles on the surface of untreated viscose fibers which have been soiled and vacuumed. In contrast, Figure 17*d* shows the presence of only a relatively few particles of soil on soiled and vacuumed viscose fibers which have been treated with Juvenon Soil Retardant R.

Oil Barrier

Soil-retardant finishes may also act in another way —by interfering with oil bonding of dirt. The finish may constitute a barrier between the fiber and the oil in the dirt, preventing their mutual attraction.

Juvenon Soil Retardant R provides an especially effective soil-resistant finish for the synthetic, hydro-

Fig. 8. Optical and electron micrographs of cotton fiber. Left, optical; right, electron.

Fig. 9. Optical micrograph of soiled cotton fiber.

phobic fibers as shown in Figures 18 and 19. These figures are plots of Improvement Factor (a photometric measure of the improvement in soil resistance of treated over untreated) versus amount of soil applied to the fabrics in a laboratory accelerated soil tester. The fabrics tested were rug samples of a standard Axminister construction. As can be seen, the soil-retardant finish gave a greater degree of improvement in soil resistance to the synthetic, hydrophobic fibers than to the rayon and wool.

Water Repellency

Probably the earliest water-repellent finish consisted of a wax emulsion. Later, combinations of wax emulsions and metallic salts of aluminum and zirconium acetate were used in order to obtain increased durability. This type of repellent is still used widely on synthetic fibers because it gives a soft, full-bodied hand in addition to water repellency. On synthetic fibers, this type of water repellent is durable to light laundering and dry cleaning. It is especially useful on fabrics such as Dynel which cannot withstand the high curing temperatures required for applying the durable water repellents because of its low melting point.

The earliest more durable water repellent contained stearamidomethyl pyridinium chloride (Zelan[5]). Soon after the introduction of Zelan, another quaternary salt, Norane,[6] was introduced. These prod-

[5] Trademark of E. I. du Pont de Nemours & Co., Inc.
[6] Trademark of Warwick Chemical Co.

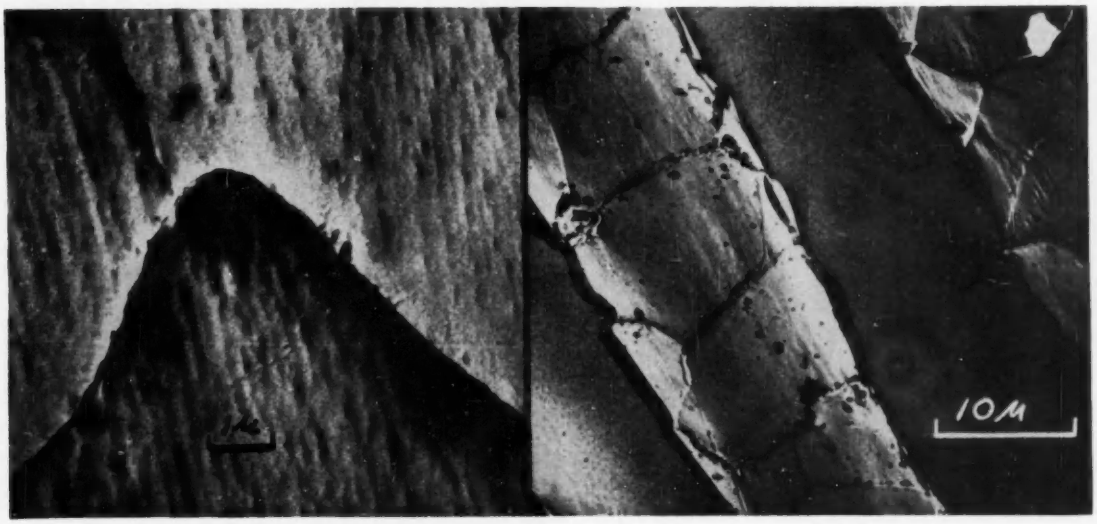

Fig. 10. Electron and optical micrographs of wool fiber. Left, electron; right, optical.

Fig. 11. Electron micrograph of soiled woolen fiber.

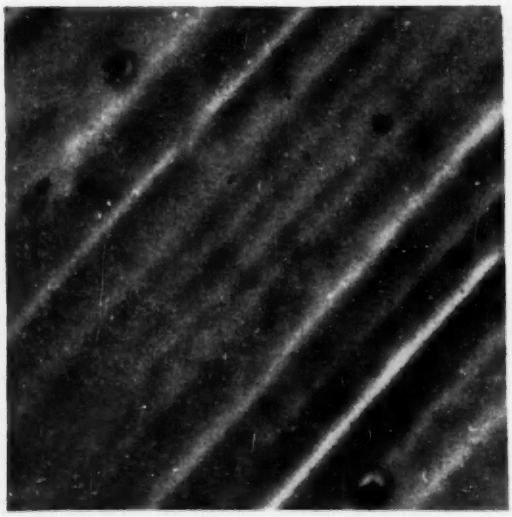

Fig. 12. Electron micrograph of nylon fiber (45,000 ×).

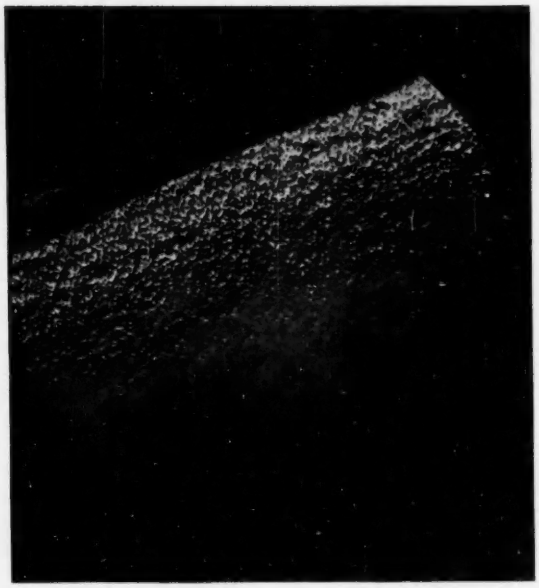

Fig. 13. Electron micrograph of polyester fiber (15,000 ×).

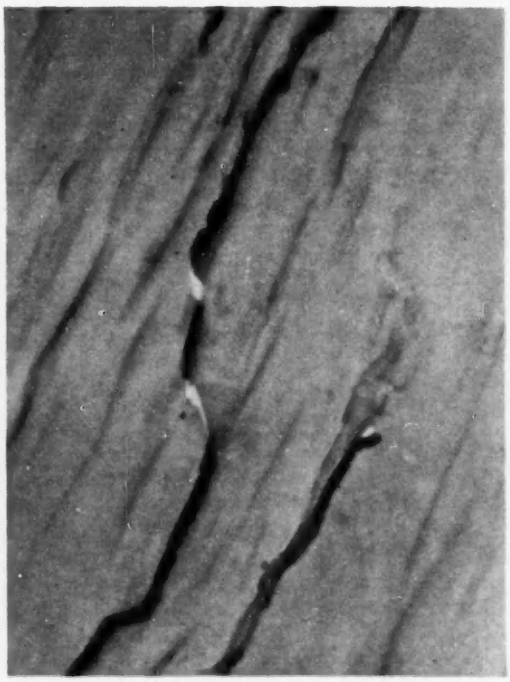

Fig. 14. Electron micrograph of acrylic fiber (20,000 ×).

ucts have been used extensively on cotton, especially for military purposes. Later, a melamine resin-based durable water repellent, Permel Resin, was introduced. This product, in combination with thermosetting resins, has found wide use in treating rayon fabrics and blends of rayon with synthetics to produce a water-repellent, wrinkle-resistant finish. It is also being used extensively with thermosetting resins on interfacing fabric to produce a firm, resilient fabric with high wrinkle recovery. It has also found increasing use on drapery and upholstery fabrics, and corduroy. Permel Resin is also used on synthetics for imparting other properties in addition to water repellency. On acetate fabrics, it has been found to reduce the gas fading properties and improve the wash fastness and light fastness of some acetate dyes. It has also given improved tear strength, sewability and abrasion resistance.

The most recently developed durable water repellent has been the silicone resin. Silicone resin has excellent durability to dry cleaning. It has found extensive use on synthetic fabrics where it gives improved tear strength, sewability, abrasion resistance, and a pleasing hand, in addition to water repellency.

Fabrics of the synthetic, hydrophobic fibers have a tendency to permit water to wick or migrate. Water-repellent treatments of fabrics containing these fibers usually overcome this wicking property.

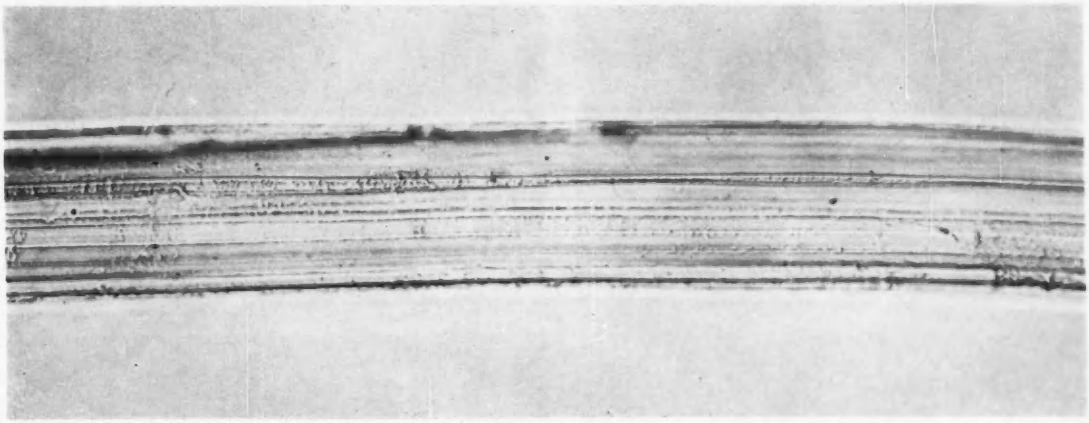

Fig. 15. Optical micrograph of serrated viscose fiber after treatment with Juvenon Soil Retardant R. For illustration of before treatment, see Figure 6.

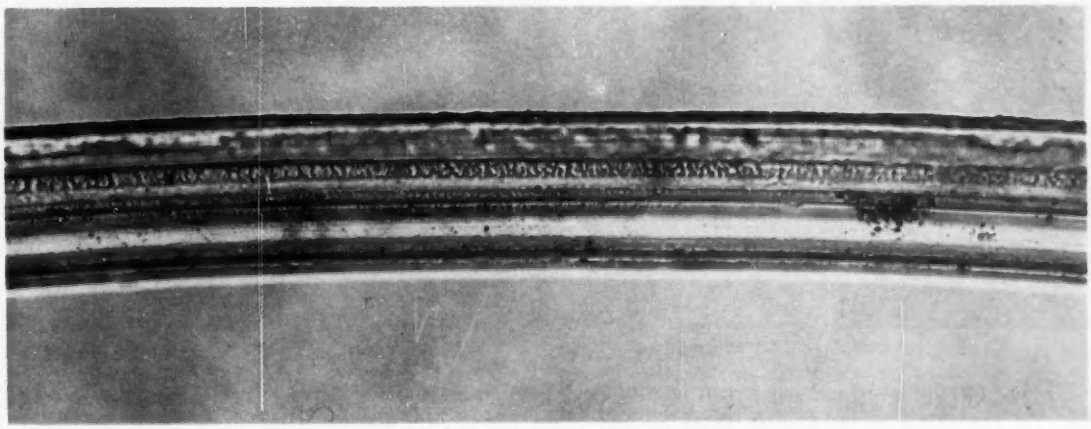

Fig. 16. Serrated viscose fibers from soiled carpets treated with Juvenon Soil Retardant R. For illustration of untreated fibers, see Figure 6.

Antistatics

The synthetic, hydrophobic fabrics such as nylon, Dacron, Orlon, Arnel[7] triacetate fiber, and Dynel generate static electricity during the processing of the fabrics and in their use. Static electricity in processing can be minimized by control of the humidity in the air, by de-ionizers and by the use of antistatic agents. Antistatic agents have been developed which have limited durability to dry cleaning and washing. Further research work is needed to develop a truly durable antistatic finish.

[7] Trademark of Celanese Corp. of America.

Shrinkage Control

Shrinkage of cotton fabrics can be controlled by the Sanforizing process which is a compressive me-

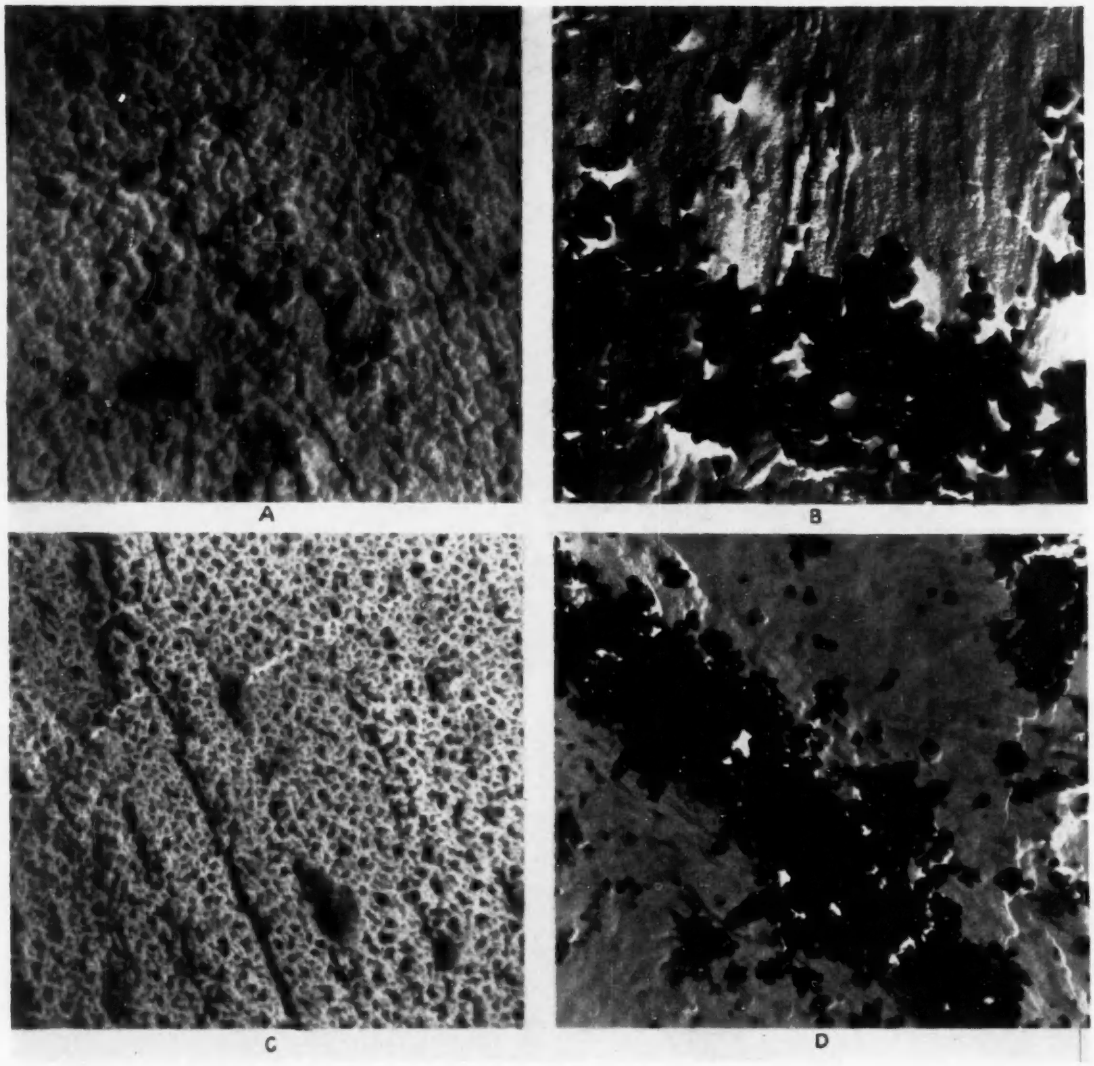

Fig. 17. Electron micrographs of serrated viscose fibers (20,000 ×). (*a* and *b*) Unsoiled viscose treated with Juvenon Soil Retardant R. (*c*) Soiled and vacuumed, untreated serrated viscose. (*d*) Soiled and vacuumed serrated viscose which had been treated with Juvenon Soil Retardant R.

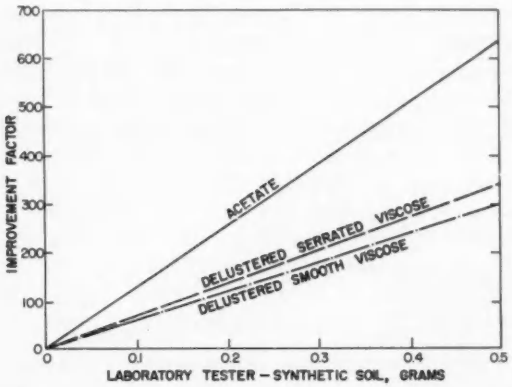

Fig. 18. Effect of Juvenon Soil Retardant R on rate of soiling of acetate and viscose carpets (laboratory test).

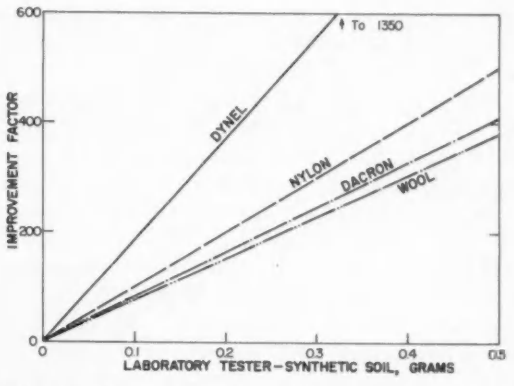

Fig. 19. Effect of Juvenon Soil Retardant R on rate of soiling of wool and man-made fibers (laboratory test).

chanical treatment. Shrinkage on rayon fabrics can be reduced by the Avcoset [8] process which involves the use of formaldehyde and a cellulose ether. Shrinkage of rayon fabrics and cotton fabrics can also be controlled by the use of thermosetting resins. Recently, thermosetting resins have been applied as additives to the Avcoset process. Shrinkage control of wool is achieved by melamine resin treatment or chlorination. Shrinkage of most of the synthetic, hydrophobic fibers is controlled by means of heat setting. Therefore, although further improvements in shrinkage control are desirable, generally satisfactory shrinkage control can be obtained by the methods given above.

Heat Resistance

The synthetic, hydrophobic fibers are thermoplastic and are therefore affected by high temperature. Many of them have the deficiency of softening at comparatively low temperatures and glazing with a hot iron. Heat setting overcomes this deficiency with many of them. For example, one of the important advantages of the triacetate over the normal acetate fiber is its ability to be heat set and thereby raise the softening point of the fiber. Another disadvantage of many of the synthetic, hydrophobic fibers is a tendency to yellow on exposure to high temperatures. Further research is needed to overcome this deficiency.

Pilling

One of the deficiencies of the synthetic, hydrophobic fibers, especially the polyesters, has been the tendency for some fabrics made from these fibers to pill. Recently, progress has been reported in the reduction of the pilling of fabrics made from Dacron by mechanical means [8]. The fabric is brushed to remove some of the loose fibers and raise others which are later removed by shearing or singeing. It has also been found that improved pilling resistance has been obtained by heat setting to allow shrinkage in both the warp and filling directions. The recommended procedure is to brush, heat set and shear, and then singe. Some fabrics, but not all, gain increased resistance to pilling when treated with thermosetting resin combinations. Although considerable progress has been made toward the reduction of pilling, further research work should be carried out in order to solve the problem of pilling which is an important deficiency of many of the synthetic, hydrophobic fibers.

Yarn Slippage

One of the problems with the synthetic, hydrophobic fibers is yarn slippage. Slippage of yarns can be reduced by the use of both thermosetting and thermoplastic resins. Also, the use of a small particle-size material such as colloidal silica has been used to some extent to reduce yarn slippage.

Hand

A soft hand can be produced on most fabrics made of synthetic fibers by the use of softeners. Most softeners are either cationic or anionic in nature and have only limited durability to either washing or dry cleaning. Water repellents of the Zelan, Permel, or silicone type have been used in increasing amounts

[8] Trademark of American Viscose Co.

in recent years to provide durable softening of fabrics. These durable softeners usually improve the tear strength and abrasion resistance of fabrics. These products have also found utility in improving sewability and reducing hole formation in fabrics made from the synthetic, hydrophobic fibers caused by heated needles during high-speed sewing. Variations in hand can be obtained with thermoplastic resin emulsions including vinyl acetate, the acrylates, and the alkyd resins. A firm hand can be obtained with most fabrics by the use of thermosetting resins. The latter resins give a dry, crisp, full hand. With the cellulosic fabrics and with nylon, this dry, crisp hand is durable to both dry cleaning and washing. It is presumed that this hand is durable on these fabrics primarily owing to the chemical reaction of the resin with the fiber. With fibers like Arnel, Orlon, Dacron, and Saran,[9] the hand produced by thermosetting resins has only limited durability to washing and dry cleaning. Further research work is needed to produce a durable firm hand on these latter fabrics.

Summary

As can be seen, considerable progress has been made in the finishing of fabrics. A number of desired properties have been obtained. Progress has been made in wrinkle resistance, wash and wear properties, soil resistance, and water repellency. Progress has also been made in the flameproofing of nylon. However, further research and development are needed to develop a satisfactory fire-resistant treatment for other synthetic, hydrophobic fibers. Further work is needed to develop durable antistatic agents. Further research is also needed to reduce the pilling of synthetic, hydrophobic fibers, and to develop a durable, stiff hand for many of them. Further developments are needed to overcome the deficiency of many of the synthetic, hydrophobic fibers of softening at comparatively low temperatures and glazing with a hot iron. Also, a means of decreasing the yellowing of many of these fibers on exposure to high temperatures is greatly needed.

Although great progress has been made in the finishing of the older fibers and considerable progress in the finishing of the newer synthetic fibers, more research in this field is indicated in order to obtain functional finishes tailor-made for specific fabric end uses. Perhaps, further work should be done on the part of the fiber manufacturers to build a chemical handle on the fiber so that functional finishes can be chemically reacted with the fiber to make them durable. Certainly the development of finishes for the newer synthetics should be a very challenging and rewarding field.

[9] Trademark of The Dow Chemical Company.

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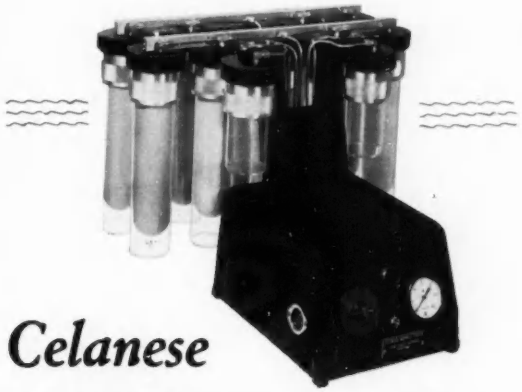
Literature Cited

1. Cogovan, E. J., and Frederici, E. D., U. S. Pat. 2,622,307 (1952).
2. Cooke, T. F., et al., "Mechanism of Imparting Wrinkle Recovery to Cellulosic Fabrics," TEXTILE RESEARCH JOURNAL **24**, 1015 (1954).
3. Florio, P. A., and Mersereau, E. P., TEXTILE RESEARCH JOURNAL **25**, 641 (1955).
4. Fortess, F., and Kip, C. E., *Am. Dyestuff Reporter* **42**, 597 (1953).
5. Getchell, N. F., TEXTILE RESEARCH JOURNAL **25**, 150 (1955).
6. Leonard, E. A., Schwartz, E. W. K., New York Section, A.A.T.C.C., *Am. Dyestuff Reporter* **41**, 322 (1952).
7. Masland II, C. H., *Rayon Textile Monthly* **20**, 573, 654 (1939).
8. Rumsey, J. S., *Papers of the American Assoc. for Textile Technology, Inc.* **27** (June 1955).
9. Saunders, H. L., and Lambert, J. M., *J. Am. Oil Chemists' Soc.* **27**, 153 (1950).
10. Schappel, J. W., Fiber Society Annual Meeting, Alabama Polytechnic Institute (May 5, 1955).
11. Snell, F. T., Snell, C. T., and Reich, I., *J. Am. Oil Chemists' Soc.* **27**, 62 (1950).
12. Stout, L. E., and Schriemeier, K. F., *Ind. Eng. Chem.* **25**, 1403 (1933).

Manuscript received December 21, 1955.



Celanese

WRINKLE TESTER

The Celanese Wrinkle Tester was developed at the Summit Research Laboratories of the Celanese Corporation of America and designed and manufactured under agreement by Custom Scientific Instruments. The Wrinkle Tester is a helpful tool in evaluating the resilience and wrinkle behavior of fabrics under conditions very similar to those occurring in actual use. This instrument takes into account that in actual wear, fabrics, due to their inherently different wrinkle resistance, display wide differences in the pattern and degree of wrinkling. The Wrinkle Tester simulates the widely accepted clenched fist test by performing a repetitive cycle wrinkling action under precisely controlled conditions.

The apparatus consists essentially of an air system which alternately pumps the air out of a group of specimen tubes into another set of specimen containers. The air system is composed of an air pump, humidifer to saturate the air with moisture in case it is desired to run the testing with high humidity.

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